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Survey of Methylene Chloride Emission Sources

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The potential health impact of methylene chloride emissions is being investigated. This document contains information on the sources of methylene chloride emissions, current emission levels, control methods that could be used to reduce methylene chloride emissions, and cost estimates for employing controls.

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Survey of Methylene Chloride Emission Sources

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

June 1985

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TABLE OF CONTENTS

TABLE OF CONTENTS iii
LIST OF TABLES. viii
LIST OF FIGURES x

Chapter Page

1.0 INTRODUCTION AND SUMMARY. 1-1

1.1 INTRODUCTION 1-1

1.2 SUMMARY. 1-2
1.2.1 MC Emission Source Categories 1-2
1.2.2 Emission Estimates. 1-3
1.2.3 Additional Control of MC Emissions. 1-6
1.2.4 Regulatory Requirements 1-7

1.3 REFERENCES 1-10

2.0 METHYLENE CHLORIDE PRODUCTION 2-1

2.1 QUANTITIES PRODUCED AND MANUFACTURERS. 2-1

2.2 PRODUCTION PROCESSES 2-3
2.2.1 Direct Chlorination of Methane. 2-3
2.2.2 Hydrochlorination of Methanol 2-4

2.3 CURRENT EMISSIONS AND CONTROLS 2-4

2.4 COST OF ADDITIONAL CONTROLS. 2-19
2.4.1 Control of Process Vent Emissions 2-19
2.4.2 Control of Equipment Leak Emissions 2-23
2.4.3 Control of Storage Emissions. 2-23
2.4.4 Control of Loading Emissions. 2-24

2.5 REFERENCES 2-25

3.0 OTHER CHEMICAL PLANTS 3-1

3.1 PROCESS DESCRIPTIONS, EMISSIONS, AND CURRENT CONTROLS 3-1

3.1.1 TRIACETATE FIBER PRODUCTION. 3-1
3.1.1.1 Process Description 3-1
3.1.1.2 Current Emissions and Controls. 3-3

3.1.2 POLYCARBONATE RESIN. 3-13
3.1.2.1 Process Description 3-13
3.1.2.2 Current Controls and Emissions. 3-13

3.1.3 RUBBER CEMENT MANUFACTURING. 3-19
3.1.3.1 Current Emissions and Controls. 3-19

3.1.4 RUBBER ACCELERATOR MANUFACTURING 3-20
3.1.4.1 Current Emissions and Controls. 3-20

TABLE OF CONTENTS (Continued)

Chapter Page

3.1.5 INSULATING MATERIALS MANUFACTURE 3-22
  3.1.5.1 Current Emissions and Controls. 3-22

3.1.6 BAYGON^{R} 1.5 MANUFACTURING. 3-22
  3.1.6.1 Current Emissions and Controls. 3-23

3.1.7 SPECIALTY CHEMICALS. 3-23
  3.1.7.1 Process Description 3-23
  3.1.7.2 Current Emissions and Controls. 3-24

3.1.8 UNIDENTIFIED PRODUCTION PROCESSES. 3-24
  3.1.8.1 Current Emissions and Controls. 3-25

3.1.9 VINYL CHLORIDE MONOMER 3-28
  3.1.9.1 Process Description 3-28
  3.1.9.2 Current Emissions and Controls. 3-28

3.1.10 PLASTICS PRODUCTION. 3-28
  3.1.10.1 Current Emissions and Controls. 3-28

3.2 COST OF ADDITIONAL CONTROL 3-30
  3.2.1 Control of Process Vent Emissions 3-31
  3.2.2 Control of Equipment Leaks. 3-31
  3.2.3 Control of Storage Emissions. 3-36

3.3 REFERENCES 3-37

4.0 SOLVENT DEGREASING OPERATIONS 4-1

4.1 INDUSTRY DESCRIPTION 4-1

4.2 DEGREASING EQUIPMENT 4-2

4.3 EMISSIONS FROM DEGREASING OPERATIONS 4-3

4.4 EMISSIONS CONTROL. 4-5

4.5 COST OF EMISSIONS CONTROL. 4-8

4.6 REGULATORY REQUIREMENTS. 4-14

4.7 REFERENCES 4-15

5.0 PHOTORESIST STRIPPING OPERATIONS. 5-1

TABLE OF CONTENTS (Continued)

Chapter Page

5.1 INDUSTRY DESCRIPTION 5-1

5.2 EMISSIONS AND CONTROL TECHNIQUES 5-2

5.3 REGULATORY REQUIREMENTS. 5-3

5.4 REFERENCES 5-5

6.0 FOAM MANUFACTURING. 6-1

6.1 INDUSTRY DESCRIPTION 6-1

6.2 CURRENT EMISSIONS AND CONTROLS 6-2

6.3 REFERENCES 6-4

7.0 PHARMACEUTICAL MANUFACTURING. 7-1

7.1 INDUSTRY DESCRIPTION 7-1

7.2 CURRENT EMISSIONS AND CONTROLS 7-2

7.3 REFERENCES 7-4

8.0 PESTICIDE MANUFACTURING 8-1

8.1 INDUSTRY DESCRIPTION 8-1

8.2 EMISSIONS AND CONTROLS 8-3

8.3 REFERENCES 8-4

9.0 DISTRIBUTION FACILITIES 9-1

9.1 EMISSIONS FROM DISTRIBUTION FACILITIES 9-1

9.2 REGULATORY REQUIREMENTS. 9-2

9.3 REFERENCES 9-4

10.0 ADDITIONAL EMISSION SOURCES OF MC 10-1

10.1 AEROSOLS 10-1

10.2 PAINT REMOVERS 10-3

TABLE OF CONTENTS (Continued)

Chapter Page

10.3 PHOTOGRAPHIC FILM PROCESSING. 10-3

10.4 FOOD PROCESSING INDUSTRY. 10-3

10.5 GENERAL MISCELLANEOUS 10-4

10.6 REFERENCES. 10-5

APPENDIX A: METHODS USED FOR ESTIMATING STORAGE TANK AND EQUIPMENT LEAK EMISSIONS A-1

A.1 EMISSION FACTORS FOR FIXED-ROOF TANKS A-1
A.1.1 Emission Equations A-1
A.1.2 Parameter Values and Assumptions A-1
A.1.3 Sample Calculation A-2

A.2 EMISSION FACTORS FOR INTERNAL FLOATING ROOF STORAGE TANKS. A-4
A.2.1 Emission Equations A-4
A.2.2 Parameter Values and Assumptions A-4
A.2.3 Sample Calculation A-7

A.3 EQUIPMENT LEAK EMISSIONS-SAMPLE CALCULATIONS. . A-10

A.4 REFERENCES. A-12

APPENDIX B: METHODS FOR ESTIMATING EMISSION CONTROL COSTS. . . . B-1

B.1 PROCESS VENT EMISSIONS CONTROL COST ESTIMATION. B-1

B.2 COST CALCULATIONS FOR INSTALLING INTERNAL FLOATING ROOFS IN FIXED ROOF TANKS. B-14
B.2.1 Capital Cost B-14
B.2.2 Annual Cost. B-15
B.2.3 MC/VOC Reduction B-15
B.2.4 Recovery Credits B-16
B.2.5 Net Annual Cost. B-16
B.2.6 Cost Effectiveness B-16

B.3 COST CALCULATIONS FOR INSTALLATION OF REFRIGERATED CONDENSERS TO CONTROL STORAGE AND LOADING EMISSIONS B-16
B.3.1 Capital Cost B-17
B.3.2 Annual Cost. B-17
B.3.3 MC/VOC Emission Reduction. B-17
B.3.4. Recovery Credit. B-18

TABLE OF CONTENTS (Continued)

Chapter Page

B.3.5 Net Annual Cost. B-18
B.3.6 Cost Effectiveness B-18

B.4 SAMPLE CALCULATIONS FOR EQUIPMENT LEAK CONTROL COSTS B-18

B.5 REFERENCES. B-22

APPENDIX C: SUMMARY OF EXISTING STATE AND FEDERAL REGULATIONS AFFECTING METHYLENE CHLORIDE EMISSION SOURCES C-1

C.1 EXISTING STATE REGULATIONS C-1
C.1.1 Introduction. C-1
C.1.2 General State VOC Regulations for Solvent Use C-1
C.1.3 Prevention of Significant Deterioration Regulations C-3
C.1.4 State Regulations Affecting Chemical Production. C-3

C.2 EXISTING FEDERAL REGULATIONS C-3

APPENDIX D: MATERIAL BALANCE FOR MC EMISSIONS OPERATIONS. D-1

D.1 MATERIAL BALANCE D-1

D.2 NATIONAL EMISSION REDUCTION CALCULATIONS D-3

D.3 PHOTORESIST STRIPPING EMISSION FACTOR. D-6

D.4 REFERENCES D-7

APPENDIX E: EMISSIONS FROM DISTRIBUTIONS FACILITIES E-1

LIST OF TABLES

Table Page

1-1 EMISSIONS FROM THE PRODUCTION AND USE OF METHYLENE CHLORIDE. 1-4

1-2 ACHIEVABLE MC EMISSION REDUCTION FOR ALL CHEMICAL PLANTS AND DEGREASERS AS A FUNCTION OF COST EFFECTIVENESS 1-8

2-1 METHYLENE CHLORIDE PRODUCERS AND PRODUCTION CAPACITIES. . 2-2

2-2 TOTAL EMISSIONS FROM METHYLENE CHLORIDE PRODUCTION FACILITIES. 2-7

2-3 CURRENT CONTROLS AND ESTIMATED EMISSIONS AT FACILITIES PRODUCING METHYLENE CHLORIDE 2-9

2-4 COST OF ADDITIONAL CONTROLS AT MC PRODUCTION FACILITIES . 2-20

2-5 ESTIMATED MC EMISSION REDUCTIONS FOR MC PRODUCTION FACILITIES AS A FUNCTION OF COST EFFECTIVENESS. 2-22

3-1 TOTAL EMISSIONS FROM CHEMICAL PLANTS USING METHYLENE CHLORIDE PRODUCTION FACILITIES 3-2

3-2 ESTIMATED EMISSIONS AND CURRENT CONTROLS AT FACILITIES USING METHYLENE CHORIDE IN PRODUCTION 3-5

3-3 COST OF ADDITIONAL CONTROLS AT CHEMICAL PLANTS USING MC IN PRODUCTION 3-32

3-4 ESTIMATED MC EMISSION REDUCTIONS FOR OTHER CHEMICAL PLANTS AS A FUNCTION OF COST EFFECTIVENESS 3-35

4-1 1983 MC EMISSIONS FROM DEGREASING OPERATIONS, BY INDUSTRY 4-4

4-2 1983 METHYLENE CHLORIDE EMISSIONS FROM DEGREASING OPERATIONS, BY STATE. 4-6

4-3 EXAMPLE CONTROL TECHNIQUES FOR DEGREASERS 4-7

4-4 RETROFIT CONTROL COSTS FOR COLD CLEANERS. 4-9

4-5 RETROFIT CONTROL COSTS FOR OPEN TOP VAPOR DEGREASERS. 4-10

4-6 RETROFIT CONTROL COSTS FOR CONVEYORIZED DEGREASERS 4-12

LIST OF TABLES (Continued)

Table Page

5-1 1983 METHYLENE CHLORIDE EMISSIONS FROM PHOTORESIST STRIPPING OPERATIONS, BY STATE. 5-4

6-1 1983 MC EMISSIONS FROM FOAM MANUFACTURING, BY STATE . . . 6-3

8-1 1983 CONSUMPTION OF METHYLENE CHLORIDE IN PESTICIDE MANUFACTURING 8-2

9-1 SUMMARY OF MAJOR METHYLENE CHLORIDE DISTRIBUTORS. 9-3

10-1 ADDITIONAL USES OF METHYLENE CHLORIDE IN 1983 10-2

A-1 PAINT FACTORS FOR FIXED-ROOF TANKS. A-3

A-2 TYPICAL NUMBER OF COLUMNS AS A FUNCTION OF TANK DIAMETERS A-5

A-3 SUMMARY OF DECK FITTING LOSS FACTORS (K_f) AND TYPICAL NUMBER OF FITTINGS (N_f) A-8

B-1 TOTAL INSTALLED CAPITAL COST AS A FUNCTION OF VENT STREAM FLOW RATE. B-2

B-2 ADDITIONAL DUCT COST. B-3

B-3 PIPE RACK COST. B-4

B-4 OPERATING FACTORS FOR EACH DESIGN CATEGORY. B-5

B-5 ANNUALIZED COST FACTORS B-6

B-6 SAMPLE CALCULATION FOR INCINERATOR COSTING. B-7

B-7 COST CONVERSION FACTORS B-13

B-8 CONTROL TECHNIQUES AND COST FOR CONTROLLING EQUIPMENT LEAK EMISSION SOURCES. B-19

C-1 GENERAL STATE VOC REGULATIONS FOR PHOTOCHEMICAL SOLVENTS. C-2

C-2 STATE REGULATIONS AFFECTING CHEMICAL PRODUCTION FACILITIES EMITTING METHYLENE CHLORIDE C-4

C-3 SUMMARY OF FEDERAL REGULATIONS AFFECTING VOLATILE ORGANIC COMPOUND EMITTING SOURCES C-5

LIST OF FIGURES

Figure		Page
2-1	Process flow diagram for the production of methylene chloride and co-products by the direct chlorination of methane.	2-5
2-2	Process flow diagram for the production of methylene chloride and co-products by the hydrochlorination of methanol	2-6
3-1	Process flow diagram for the production of triacetate fiber	3-4
3-2	Process flow diagram for the production of polycarbonate resin	3-14

1.0 INTRODUCTION AND SUMMARY

1.1 INTRODUCTION

This document identifies the sources and locations of methylene chloride (MC) emissions, estimates total 1983 production and consumption volumes, estimates emission levels, identifies applicable control techniques for each source, and estimates the cost effectiveness of controlling emissions for selected sources. The information collected in this source assessment study will also be used by the U.S. Environmental Protection Agency (EPA) to estimate human exposure to MC.

Information for this document was acquired from various sources. Background information, such as previous EPA documents and other published literature, was reviewed in an attempt to identify the producers of MC and the major applications. Four companies producing MC at six facilities were identified. Also, two companies producing polycarbonate resins and one company producing triacetate fibers were identified. Letters were sent to these seven companies under the authority of Section 114 of the Clean Air Act requesting information concerning MC emissions, emission levels, and control techniques for all possible emission sources associated with the production, storage, and use of MC in the calendar year 1983. General information such as production volumes and total sales/purchase data were also requested in order to verify the completeness of the submitted information. The production and sales/purchase information was requested to be treated as confidential and is not discussed in this report. For each process unit making or consuming MC, detailed information was requested on the following emission types: process vent emissions, equipment leaks, equipment opening losses, raw material/product storage emissions, loading/handling emissions, and secondary emissions (i.e. emissions as a result of treating or disposing of plant waste streams). The companies were asked only to estimate these emissions. No testing was required specifically for this information request.

Plant trips were taken to Vulcan Chemicals in Geismar, Louisiana; Dow Chemical U.S.A. in Plaquemine, Louisiana; and General Electric in Mt. Vernon, Indiana to gain familiarity with the processes, emission sources, and emission controls at these facilites. Meetings were held with plant representatives to discuss operating procedures, the process equipment used, potential emission sources, and methods of emissions control.

The predominant uses of MC are as a constituent in aerosols and paint removers. Since aerosols and paint removers are largely consumer products, it was assumed that associated emissions are proportional to general population distribution in the U.S. Other significant uses of MC that were identified include solvent degreasing, chemical production, foam manufacturing, pharmaceutical manufacturing, pesticide manufacturing and photoresist stripping. Information for chemical plants was obtained directly through Section 114 requests. For the other significant MC use categories, no attempt was made to identify the locations of all facilities using MC. However, information was obtained from the Halogenated Solvents Industry Alliance (HSIA), a trade group representing the producers of MC and other halogentated solvents, regarding the total amount of MC used in 1983 for all known applications. Using HSIA and other available information, emission levels in 1983 were estimated for each application.

1.2 SUMMARY

1.2.1 MC Emission Source Categories

Methylene chloride is produced by four companies at six plants in the United States. The estimated total 1983 production volume of MC was 240,000 Mg[1]. Two processes are used to produce MC: (1) hydrochlorination of methanol, and (2) chlorination of methane. In 1983, the disposition of MC was as follows: aerosols (22 percent), paint removers (28 percent), degreasing operations (9 percent), foam manufacturing (7 percent), pharmaceutical manufacturing (6 percent), photoresist stripping operations (5 percent), film processing (3 percent), food processing (1 percent), and pesticide manufacturing (1 percent).

Additional applications include general miscellaneous uses such as a solvent in the printing industry, as a thinning agent for adhesives, as a solvent in cleaning solutions, and as a solvent or reactant in the chemical processing industry. Individual consumption levels are not known for these general uses. Their combined consumption was 5 percent of total use.

Emission estimates have been made in this study for the following categories: MC production facilities, chemical plants, degreasing operations, photoresist stripping operations, foam manufacturing, pharmaceutical manufacturing, pesticide manufacturing, distribution facilities, aerosols, paint removers, photographic film processing, food processing, and the general miscellaneous applications.

1.2.2 Emission Estimates

The total emissions from MC production and use in 1983 are estimated to be 197,500 Mg/yr. The largest sources of MC emissions were paint removers (62,000 Mg/yr), aerosols (52,900 Mg/yr), degreasing operations (17,700 Mg/yr), foam manufacturing (14,200 Mg/yr), and photoresist stripping operations (6,800 Mg/yr). The source categories and emissions are presented in Table 1-1.

Methylene chloride emissions from MC production processes are estimated to be 770 Mg/yr. MC emissions from miscellaneous chemical production processes using MC are estimated to be 10,700 Mg/yr. The chemical products of these processes include triacetate fibers, polycarbonate resins, plastics, rubber cement, rubber accelerators, insulating materials, specialty chemicals, vinyl chloride, and BAYGON^R 1.5 (pesticide). The estimate of total emissions from MC producing plants and other chemical plants was obtained from information provided by these facilities in response to Section 114 requests. These plants provided emission estimates from process vents (estimated at full capacity), loading/handling operations, equipment opening losses, pressure relief valve discharges, and secondary streams. The chemical plants also provided counts of all equipment (such as pumps, valves, and flanges) in MC service and data on the number and types of product/raw

TABLE 1-1. EMISSIONS IN 1983 FROM THE PRODUCTION AND USE OF METHYLENE CHLORIDE

Emission Source	Production/Consumption (Mg/yr)	Emissions (Mg/yr)
MC Production	240,000	770
Other Chemical Production	N/A	10,700[b]
Degreasing Operations	21,300	17,700
Photoresist Stripping Operations	11,900	6,800
Foam Manufacturing	14,200	14,200
Pharmaceutical Manufacturing	13,200	5,700
Pesticide Manufacturing	2,700	2,700
Distribution Facilities	218,000[a]	500
Aerosols	52,900	52,900
Paint Removers	62,000	62,000
Photographic (film processing)	8,100	8,100
Food Processing	3,330	3,300
Miscellaneous	12,100	12,100
TOTAL	-	197,500

[a] Estimated amount of MC sold through distribution.
[b] Based on update of preliminary information provided by chemical plants.
N/A = Not Available

material storage tanks containing MC. Total volatile organic compound (VOC) emissions from equipment leaks were calculated by applying the Synthetic Organic Chemical Manufacturing Industry (SOCMI) VOC equipment leak emission factors to the equipment counts.[2] MC emissions were estimated in a similar manner except that the fraction of MC in the stream for each piece of equipment was applied to the calculated VOC emissions. Emissions from storage tanks were estimated by using AP-42 equations and storage tank data supplied by each company.[3] Methods for estimating these emissions are described in Appendix A.

Methylene chloride emissions from degreasing operations were estimated to be 17,700 Mg in 1983. Degreasing emission estimates were made using HSIA information on 1983 MC consumption in various degreasing applications and available emission factors. The HSIA indicated that MC was used as a degreasing solvent in five major industry groups in 1983. These are: furniture and fixtures (Standard Industrial Classification (SIC)25), fabricated metal products (SIC 34), electric and electronic equipment (SIC 36), transportation equipment (SIC 37), and miscellaneous industries (SIC 39). Emission factors for degreasing operations were obtained from previous EPA studies.

MC emissions from photoresist stripping operations were estimated to be 6,800 Mg in 1983. Emissions were estimated using 1983 consumption data provided by HSIA and emissions factors derived for the printed circuit board manufacturing industry, in which photoresist stripping operations occur.

Almost all of the MC produced is sold through various chemical distributors. The handling and storage operations at distribution facilities located throughout the country were estimated to account for 500 Mg of TCE emissions in 1983.

Emissions of MC from foam manufacturing were estimated to be 14,200 Mg in 1983. Emission estimates were made using 1983 consumption data for foam manufacturing provided by the HSIA. It was assumed that all the MC used in foam manufacturing is emitted.

Emissions of MC from pharmaceutical manufacturing were estimated to be 5,700 Mg in 1983. Emissions were estimated using 1983 consumption data for pharmaceutical manufacturing provided by HSIA and an emission factor for pharmaceutical manufacturing obtained in a previous EPA study.

Emissions of MC from pesticide manufacturing were estimated to be 2,700 Mg in 1983. Emissions were estimated from 1983 consumption data for pesticide manufacturing provided by HSIA. It was assumed that all the MC consumed in pesticide manufacturing during 1983 was emitted.

Emissions of MC from photographic film processing were estimated to be 8,100 Mg in 1983. Emissions were estimated from 1983 consumption data for film processing provided by HSIA. It was assumed that all the MC consumed in photographic film processing during 1983 was emitted.

Emissions of MC from food processing were estimated to be 3,300 Mg in 1983. This estimate was based as 1983 consumption data for food processing provided by HSIA, assuming all MC consuming in food processing during 1983 was emitted.

Emissions of MC from the aggregated general miscellaneous source category were estimated to be 12,100 Mg in 1983. HSIA indicated 12,100 Mg was the consumption level of MC for the combined miscellaneous sources. It was assumed that all MC consumed in those applications is emitted.

1.2.3 Additional Control of MC Emissions

The cost associated with additional control of MC emissions was estimated for MC production plants, other chemical plants and degreasers. Due to the large number of degreasers, no attempt was made to develop cost estimates for each degreaser actually in use. Instead, cost estimates were developed for model degreasers. National costs and national emission reductions associated with controlling degreasers were based on model degreaser data. Specific information was provided for MC production and other chemical production facilities. This information was used to develop national costs and emission reduction estimates were made for these production facilities. The methodology for estimating control costs is presented in Appendix B.

Emissions of MC from chemical plants producing or using MC can be reduced by various technically feasible controls. Process vent emissions can be controlled by incineration. Equipment leak emissions can be reduced through a combination of leak detection and repair programs and application of equipment control devices. Storage tank emissions can be reduced by installation of floating roofs in fixed roof tanks. Where floating roofs are not technically feasible (i.e. horizontal tanks or extremely small diameter tanks), a refrigerated condenser can be used for control of storage emissions. Loading emissions can be controlled by venting displaced vapors to a refrigerated condenser.

Emissions of MC from degreasers can be reduced by using covers for degreasers openings, increasing degreaser freeboard area, adding freeboard chillers, providing drainage racks for parts, and installing carbon adsorbers. The methodology for estimating cost effectiveness of degreaser emission control is presented in Chapter 4.

Costs were estimated for the above control techniques for all emission sources from chemical plants and degreasers which are not presently well controlled. These costs estimates are based on the information provided in the company Section 114 responses on the emission stream and process equipment parameters and also on the data for model degreasers. It is estimated that about 11,300 Mg/yr MC emissions can be controlled by the application of control techniques on process vent, fugitive, storage tanks, and handling emissions and by application of control techniques on uncontrolled degreasers. This represents an overall emission reduction of about 39 percent over current estimated emissions from chemical production and degreasing. Table 1-2 shows the emission reduction for each emission type for various ranges of cost effectiveness.

1.2.4 Regulatory Requirements

The plants that produce MC or use it in production processes are located in 13 States: West Virginia, Texas, Louisiana, Kansas, Massachusetts, Indiana, New York, South Carolina, Pennsylvania, California Ohio, Missouri, and Michigan. Emissions from these existing chemical production facilities are not controlled by Federal regulations

TABLE 1-2. ACHIEVABLE MC EMISSION REDUCTION FOR ALL CHEMICAL PLANTS AND DEGREASERS AS A FUNCTION OF COST EFFECTIVENESS

	Nationwide MC Emission Reduction, Mg/Yr					
Cost Effectiveness Range, $/Mg of VOC	Process Vents	Equipment Leak	Storage Tanks	Loading	Degreasing	Total
Credit	864	-	182	-	-	1,050
0-500	1,940	339	47.8	-	4,130	6,460
501-1000	-	69.7	10.9	-	-	81
1001-2000	82.4	25.4	33.6	51.9	2,460	2,650
2001-5000	132	1.2	18.3	73.2	-	225
> 5000	851	-	13.8	16.9	-	882
TOTAL	3,870	435	307	142	6,590	11,300

such as the new source performance standards (NSPS) for volatile organic compounds (VOC) in the synthetic organic chemical manufacturing industry (SOCMI) because these regulations are designed to cover new, modified, or reconstructed sources.

The emissions of MC from chemical plants are controlled in only two (Pennsylvania, and Michigan) of the 11 States where MC is produced or used in production processes. MC is exempt from VOC regulations in the other States because of its negligible photochemical reactivity with the exception of Massachusetts where MC emissions from specific sources such as metal coating are regulated. However, Massachusetts regulations do not impact chemical plants.

Michigan has adopted regulations controlling storage of organic compounds having a true vapor pressure between 1.5 psia and 11 psia in existing stationary vessels of more than 40,000 gallon capacity. The vapor pressure of MC at 20°C (68°F) is approximately 6.75 psia. The regulations require that the storage tank is a pressure tank, be equipped with a floating cover with closure seal or seals, or be equipped with a vapor recovery system capable of 90 percent recovery. Pennsylvania regulations require storage tanks with a volume below 40,000 gallons to be equipped with pressure relief devices; for tanks above 40,000 gallons the regulations require a floating roof and vapor recovery system.

VOC emissions from loading/handling emissions are regulated by Michigan. The state regulation requires loading facilities handling 5,000 gal/year or more of VOC (with a true vapor pressure equal to 1.5 psia) to have submerged fill pipes.

There are no Federal regulations for MC emissions from degreasing operations. A CTG for organic solvent cleaners has been issued by EPA establishing RACT guidelines that have been used by State agencies to develop SIPs. Thirty-two States and the District of Columbia have adopted RACT for use of MC in degreasing operations. Eighteen States have not adopted any regulations. Further details on State regulations are presented in Appendix C.

1.3 REFERENCES

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3. Compilation of Air Pollutant Emission Factors, 3rd Edition. U. S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Monitoring and Data Analysis Division. Research Triangle Park, N.C. January 1984.

2.0 METHYLENE CHLORIDE PRODUCTION

This chapter presents the emissions and controls associated with the production of methylene chloride (MC) at the six production facilities in the United States. Methylene chloride is produced by the hydrochlorination of methanol at all six of these plants and by the direct chlorination of methane at one of these plants. Emission sources in MC production facilities are process vents, equipment leaks, equipment openings, relief devices, storage tanks, secondary sources, and truck, rail-car, drum, or barge loading.

2.1 QUANTITIES PRODUCED AND MANUFACTURERS

Methylene Chloride is currently produced by four companies at six plants. The estimated total production capacity of these plants is 358,000 Mg/yr.[1] In 1983 about 240,000 Mg of methylene chloride was produced.[1] The total imports of methylene chloride in 1983 were 20,000 Mg, and the total exports were 32,700 Mg indicating a domestic United States demand of about 228,000 Mg in 1983.[1] The producers, their capacities, and production processes are listed in Table 2-1.

Methylene Chloride consumption declined approximately 14 percent from 1979 to 1983.[1] This is because several MC end uses such as paint stripping, aerosols, and metal and plastic processing consumption levels decreased during the economic downturn. However, in 1984 MC demand level was 252,000 Mg, showing a 10.5 percent growth over 1983.[2] Also in 1984, imports increased to 30,000 Mg, 50 percent higher than in 1983.[2] The import surge upset the traditional trade surplus of U.S. MC but tightening chlorine availability in Europe is expected to drop imports in 1985.[2] Current predictions for future growth are in the 2 to 3 percent range.[1,2]

TABLE 2-1. METHYLENE CHLORIDE PRODUCERS AND PRODUCTION CAPACITIES

Company	Location	Process	Capacity[a] (Mg/yr) (1984)
Diamond Shamrock Corporation	Belle, WV	Hydrochlorination of methanol	50,000
Dow Chemical U.S.A.	Freeport, TX	Hydrochlorination of methanol	91,000
	Plaquemine, LA	Hydrochlorination of methanol	86,000
LCP Chemicals	Moundsville, WV	Hydrochlorination of methanol	36,000
Vulcan Materials Co.	Geismar, LA	Hydrochlorination of methanol	36,000
	Wichita, KS	Hydrochlorination of methanol Chlorination of methane	59,000[b]
TOTAL			358,000

[a] Estimated capacities from Mannsville Chemical Products Corporation.
[b] Combined capacity for both processes.

2.2 PRODUCTION PROCESSES

The two basic methods of methylene chloride production, direct chlorination of methane and hydrochlorination of methanol, differ primarily in the initial feedstock. Both processes produce methyl chloride as an intermediate. Methylene chloride is then produced by the direct chlorination of methyl chloride.

All six plants produce MC by the hydrochlorination of methanol. In addition, Vulcan/Wichita uses the direct chlorination of methane to produce about 33 percent of their MC output.[3]

2.2.1 Direct Chlorination of Methane.[4]

Methyl chloride, methylene chloride, chloroform, and carbon tetrachloride are co-produced via the direct chlorination of methane. Methane is mixed with chlorine and fed to a chlorination reactor where all four co-products are produced. The co-products are then separated by distillation. After separation the methyl chloride can be recycled to the chlorinator. The reaction conditions and the amount of methyl chloride recycled to the chlorination reactor can be controlled to yield predominantly methylene chloride. The chlorination process occurs according to the reactions:

$$\underset{\text{(methane)}}{CH_4} + \underset{\text{(chlorine)}}{Cl_2} \longrightarrow \underset{\text{(methyl chloride)}}{CH_3Cl} + \underset{\text{(hydrogen chloride)}}{HCl}$$

$$\underset{\text{(methyl chloride)}}{CH_3Cl} + \underset{\text{(chlorine)}}{Cl_2} \longrightarrow \underset{\text{(methylene chloride)}}{CH_2Cl_2} + \underset{\text{(hydrogen chloride)}}{HCl}$$

$$\underset{\text{(methylene chloride)}}{CH_2Cl_2} + \underset{\text{(chlorine)}}{Cl_2} \longrightarrow \underset{\text{(chloroform)}}{CHCl_3} + \underset{\text{(hydrogen chloride)}}{HCl}$$

$$\underset{\text{(chloroform)}}{CHCl_3} + \underset{\text{(chlorine)}}{Cl_2} \longrightarrow \underset{\text{(carbon tetrachloride)}}{CCl_4} + \underset{\text{(hydrogen chloride)}}{HCl}$$

The reactions are usually carried out at about 350°C to 370°C (660°F to 700°F) and at a pressure slightly above one atmosphere. The process flow diagram is shown in Figure 2-1.

2.2.2 Hydrochlorination of Methanol[4]

Methyl chloride is produced via the hydrochlorination of methanol, the reaction of hydrochloric acid with methanol in the liquid phase and in the presence of a catalyst at about 340°C (644°F). The direct chlorination of methyl chloride then produces methylene chloride and chloroform as co-products, and carbon tetrachloride as a by-product. The chlorination processes occur according to the reactions:

$$\underset{\text{(methanol)}}{CH_3OH} + \underset{\text{(hydrochloric acid)}}{HCl} \xrightarrow[\text{liquid phase}]{\text{catalyst}} \underset{\text{(methyl chloride)}}{CH_3Cl} + \underset{\text{(water)}}{H_2O}$$

$$\underset{\text{(methyl chloride)}}{CH_3Cl} + \underset{\text{(chlorine)}}{Cl_2} \longrightarrow \underset{\text{(methylene chloride)}}{CH_2Cl_2} + \underset{\text{(hydrochloric acid)}}{HCl}$$

$$\underset{\text{(methylene chloride)}}{CH_2Cl_2} + \underset{\text{(chlorine)}}{Cl_2} \longrightarrow \underset{\text{(chloroform)}}{CHC13} + \underset{\text{(hydrogen chloride)}}{HCl}$$

$$\underset{\text{(chloroform)}}{CHCl_3} + \underset{\text{(chlorine)}}{Cl_2} \longrightarrow \underset{\text{(carbon tetrachloride)}}{CCl_4} + \underset{\text{(hydrogen chloride)}}{HCl}$$

Cuprous chloride, activated charcoal, or zinc chloride on pumice is used as catalyst in the hydrochlorination reaction. A process flow diagram is shown in Figure 2-2.

2.3 CURRENT EMISSIONS AND CONTROLS

Emission sources and emission levels for each facility producing methylene chloride are summarized in Table 2-2. A more detailed discussion of emission sources including controls, and control

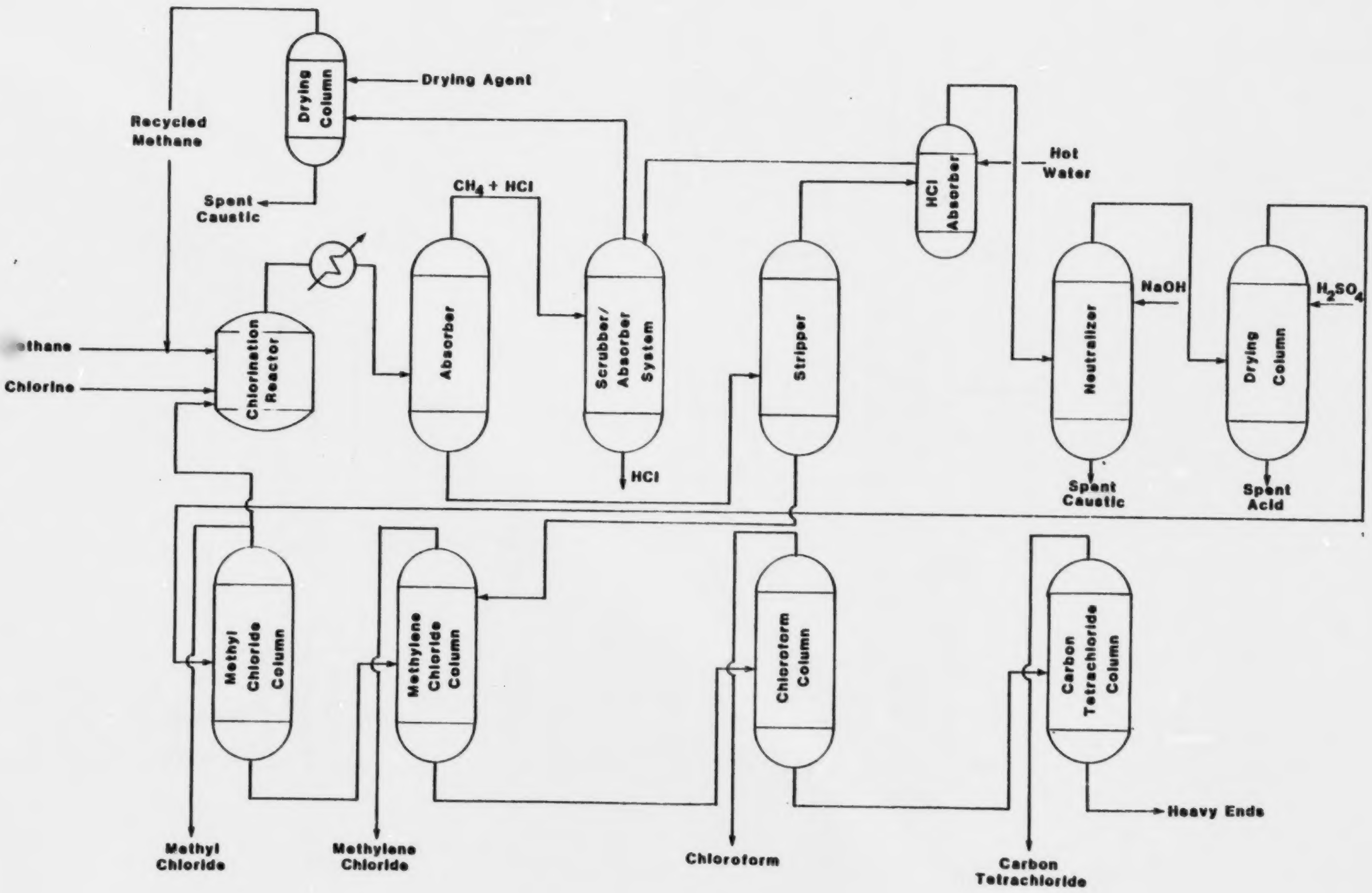
Recycled Methane
Drying Column
Drying Agent
Spent Caustic
CH$_4$ + HCl
HCl Absorber
Hot Water
ethane
Chlorine
Chlorination Reactor
Absorber
Scrubber/ Absorber System
Stripper
Neutralizer
NaOH
Drying Column
H$_2$SO$_4$
HCl
Spent Caustic
Spent Acid
Methyl Chloride Column
Methylene Chloride Column
Chloroform Column
Carbon Tetrachloride Column
Heavy Ends
Methyl Chloride
Methylene Chloride
Chloroform
Carbon Tetrachloride

Figure 2-1. Process flow diagram for the production of methylene chloride and co-products by the direct chlorination of methane.

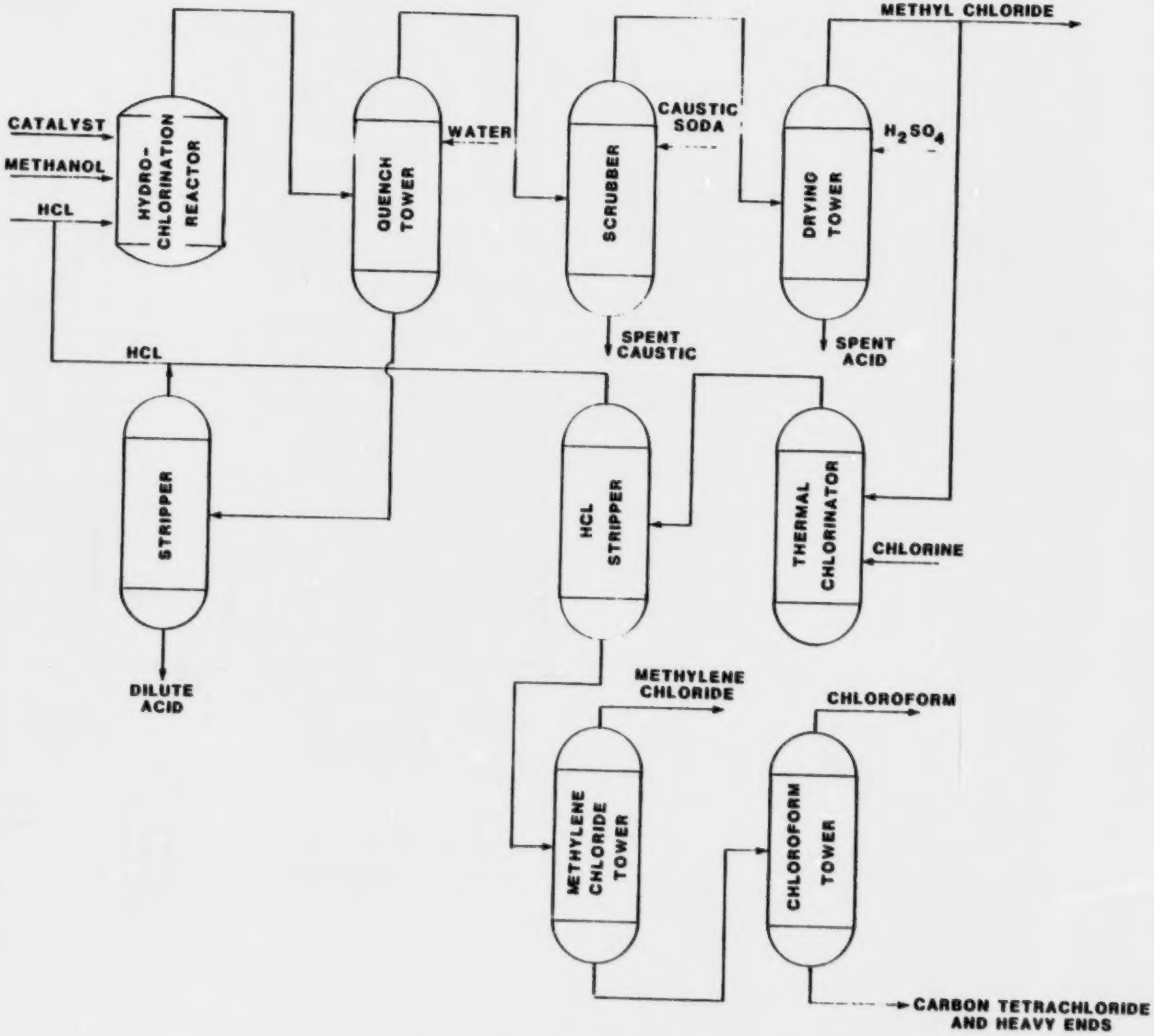
METHYL CHLORIDE
CATALYST
METHANOL
HCL
HYDRO-
CHLORINATION
REACTOR
QUENCH
TOWER
WATER
SCRUBBER
CAUSTIC
SODA
DRYING
TOWER
H_2SO_4
SPENT
CAUSTIC
SPENT
ACID
HCL
STRIPPER
HCL
STRIPPER
THERMAL
CHLORINATOR
CHLORINE
DILUTE
ACID
METHYLENE
CHLORIDE
CHLOROFORM
METHYLENE
CHLORIDE
TOWER
CHLOROFORM
TOWER
CARBON TETRACHLORIDE
AND HEAVY ENDS

Figure 2-2. Process flow diagram for the production of methylene chloride and co-products by the hydrochlorination of methanol

TABLE 2-2 TOTAL EMISSIONS FROM METHYLENE CHLORIDE PRODUCTION FACILITIES

Plant/Location	1983 Methylene Chloride Emissions (Mg/yr)							
	Process	Equipment Leaks	Relief Devices	Storage[b]	Handling	Equipment Openings	Secondary	TOTAL
Diamond Shamrock Belle, WV	5.7	75.2	3.4	26.1	4.2	1.1	0.7	116
Dow Chemical Freeport, TX	-	87.3	-	18.3	4.2	.05	0.8	111
Dow Chemical Plaquemine, LA	-	27.5	.05	73.5	115	0.6	.02	217
LCP Chemicals Moundsville, WV	84.4	28.5	0.5	21.1	23.7	0.9	6.4	165
Vulcan Materials Geismar, LA	0.7	35.5	.01	19.3	8.2	0.6	3.9	68.2
Vulcan Materials Wichita, KS	12.3	38.1	-	32.2	6.2	0.8	-	89.6
TOTAL	103	292	4.0	190	162	4.1	11.8	770

[a] Based on equipment count provided by plants and SOCMI fugitive emission factors.

[b] Based on storage tank information provided by plants and AP-42 equations.

efficiencies is presented below and shown in Table 2-3. Equipment leak, storage tank, and handling emissions account for the majority of the methylene chloride emissions from these facilities. Process vent, equipment opening, relief device, and secondary emissions were also reported by the six plants.

Dow Chemicals U.S.A. - Freeport, TX[5]

The production of methylene chloride by hydrochlorination of methanol at this facility resulted in total emissions of methylene chloride of 111 Mg in 1983. Equipment leaks accounted for a majority of these emissions, totalling 87.3 Mg/yr. The largest sources of equipment leaks were valves, flanges, and pressure relief devices. Emissions from valves were approximately 42 Mg/yr (48 percent of total equipment leaks). Seventeen percent of the equipment leaks were from flanges. Pressure relief devices constituted 19 percent of these emissions. Dow reported that inspection programs were in place for monitoring equipment leaks. These programs include routine inspection of equipment during each shift, a pressure vessel inspection program, an annual leak survey, and continuous corrosion rate monitoring. Since no repair frequency was reported, no control efficiency could be estimated for Dow's inspection program. Therefore, equipment leak emission estimates assume no control. This may overstate somewhat Dow's equipment leak emissions.

The Texas Air Control Board has recently promulgated regulations that will require a formal monitoring and repair program for volatile organic compound equipment leaks. The first round of monitoring must be completed by the end of 1987. The regulation will require the periodic testing of all valves in VOC service with a portable hydrocarbon meter, capping of open-ended lines and valves, monitoring of pump seals, and detailed record keeping of these practices. Methylene Chloride is excluded from these regulations and from other regulations governing volatile organic compounds in Texas because of its low photochemical reactivity. However, Dow would be covered by Texas regulations where MC streams are mixed with regulated volatile organic compounds (such as methyl chloride, chloroform, and carbon tetrachloride).

TABLE 2-3. CURRENT CONTROLS AND ESTIMATED EMISSIONS AT FACILITIES PRODUCING METHYLENE CHLORIDE

Company/Location	Type of Emission/ Source	Present Controls	Reported Control Efficiency	Present MC Emissions (Mg/yr)	Comments
Diamond Shamrock Belle, WV	Process				
	o Regeneration Vent	None	0	3.8	
	o Vent Recovery System 1	Condenser	68.5	1.1	
	o Vent Recovery System 2	Condenser	26.7	0.8	
	Equipment Leaks	None	0	75.2	Visual inspection
	Storage				
	o Fixed-Roof Tank	Conservation Vent Water Cooled Condenser	62.4	1.8	15,000 gallons
	o Fixed-Roof Tank	Conservation Vent Water Cooled Condenser	86.7	0.8	20,000 gallons
	o Fixed-Roof Tank	Conservation Vent Water Cooled Condenser	86.7	0.8	20,000 gallons
	o Fixed-Roof Tank	Conservation Vent Water Cooled Condenser	86.7	0.4	17,000 gallons
	o Fixed-Roof Tank	None	0	0.4	15,000 gallons
	o Fixed-Roof Tank	None	0	2.9	15,000 gallons
	o Fixed-Roof Tank	Conservation Vent Water Cooled Condenser	41.9	5.3	20,000 gallons
	o Fixed-Roof Tank	Conservation Vent Water Cooled Condenser	41.9	5.3	20,000 gallons
	o Fixed-Roof Tank	None	0	0.1	900 gallons
	o Fixed-Roof Tank	None	0	0.04	2,350 gallons
	o Fixed-Roof Tank	None	0	0.04	250 gallons
	o Fixed-Roof Tank	None	0	0.08	550 gallons
	o Fixed-Roof Tank	None	0	0.9	20,000 gallons
	o Fixed-Roof Tank	None	0	1.0	20,000 gallons
	o Fixed-Roof Tank	Conservation Vent Water Cooled Condenser Refrigerator Condenser	90.7	4.4	500,000 gallons
	o Fixed-Roof Tank	Conservation Vent Water Cooled Condenser	62.4	1.8	15,000 gallons
	Equipment Opening	None	0	1.1	12 major 150 minor
	Handling				
	o Tank cars, tank trucks	None	0	0.3	Dome loading
	o Barges	None	0	3.9	Bottom loading

(Continued)

TABLE 2-3 CONTINUED. CURRENT CONTROLS AND ESTIMATED EMISSIONS AT FACILITIES PRODUCING METHYLENE CHLORIDE

Company/Location	Type of Emission/ Source	Present Controls	Reported Control Efficiency	Present MC Emissions (Mg/yr)	Comments
	Secondary				
	o Wastewater Treatment Influent	Steam Strip/Carbon Adsorp.	N/R	0.05	
	o Solid Waste Drumming	Landfill	N/R	0.43	
	o Sludge Disposal	Off-site Treatment	N/R	0.24	
	Relief Devices	N/A		3.4	Relief Valve
Dow Chemical Freeport, TX	Equipment Leaks	None	0	87.3	Routine Freeport, inspection programs
	Storage				
	o *	*	*	18.3	
	Equipment Opening	None	0	0.05	216 openings, large vessels cleared to 200 ppm organics
	Handling				
	o Tank trucks, tank cars, ships, barges	None	0	4.2	Open dome loading
	o Drums	Flume vacuum system	N/R	N/R	
	Secondary				
	o Wastewater rain and washdown	Nonbiological Treatment	0	0.8	
	o Spent Filter Elements	Material and Energy Recovery Unit	N/R		
Dow Chemical Plaquemine, LA	Equipment Leaks	None	0	27.5	Continuous Air Monitoring
	Storage				
	o Fixed-Roof Tank	None	0	6.3	126,500 gallons
	o Fixed-Roof Tank	None	0	2.7	56,000 gallons

(Continued)

TABLE 2-3 CONTINUED. CURRENT CONTROLS AND ESTIMATED EMISSIONS AT FACILITIES PRODUCING METHYLENE CHLORIDE

Company/Location	Type of Emission/ Source	Present Controls	Reported Control Efficiency	Present MC Emissions (Mg/yr)	Comments
	o Fixed-Roof Tank	None	0	12.0	187,900 gallons
	o Fixed-Roof Tank	None	0	23.4	48,000 gallons
	o Fixed-Roof Tank	None	0	23.4	48,000 gallons
	o Contact Internal Floating-Roof	N/A	N/A	5.7	507,600 gallons
	Equipment Opening	None	0	0.6	54 Openings
	Handling o tank truck, tank car, barges	None	0	115	Dip pipe loading
	Secondary o Not identified	None	0	0.02	
	Relief Devices	N/A	0	0.05	Reactor Discharge
LCP Chemicals Moundsville, WV	Process o Purge Condenser	Compression and Condensation	b	84.3	
	o Recovery Tank	None	0	0.05	
	Equipment Leaks	None	N/R	28.5	Sampling Program
	Storage o Fixed-Roof Tank	None	0	1.3	13,600 gallons
	o Fixed-Roof Tank	None	0	1.3	13,600 gallons
	o Fixed-Roof Tank	None	0	1.3	13,600 gallons
	o Fixed-Roof Tank	None	0	4.3	51,456 gallons
	o Fixed-Roof Tank	None	0	10.7	100,455 gallons
	o Fixed-Roof Tank	None	0	1.7	18,260 gallons
	o Fixed-Roof Tank	None	0	0.5	4,750 gallons
	Handling o Rail cars, truck	None	0	23.7	Splash Fill
	Secondary o Not identified	Distillation and Recovery	N/R	1.3	
	o Not identified	Neutralization and Carbon Adsorp.	N/R	0.6	
	o Not identified	Off-site	N/R	4.5	
	Relief Devices	N/A		0.5	Reactor Overpressurization (7 times)

(Continued)

TABLE 2-3 CONCLUDED. CURRENT CONTROLS AND ESTIMATED EMISSIONS AT FACILITIES PRODUCING METHYLENE CHLORIDE

Company/Location	Type of Emission/ Source	Present Controls	Reported Control Efficiency	Present MC Emissions (Mg/yr)	Comments
Vulcan Chemicals Geismar, LA	Process Vent o *	*	*	0.7	
	Equipment Leaks	*	*	35.5	
	Storage	*	*	19.3	
	Equipment Opening	*	*	0.6	
	Handling	*	*	8.2	
	Secondary	*	*	3.9	
	Relief Devices	*	*	0.01	
Vulcan Chemicals[a] Wichita, KS	Process Vent o *	*	*	12.3	
	Equipment Leaks	*	*	38.1	
	Storage o *	*	*	32.2	
	Equipment Opening	*	*	0.8	
	Handling	*	*	6.2	

*This information is considered by the company to be confidential.

[a] Company reported greater than 98 percent control, but 98 percent was used in the absence of supporting test data.

N/A = Not applicable.
N/R = Not reported.

Losses from product storage were approximately 18.3 Mg/yr. All information concerning storage facilities and controls is considered confidential by Dow. Since methylene chloride is excluded from regulation in Texas, no state storage tank regulations are applicable to the Dow plant.

Losses due to handling were approximately 4.2 Mg/yr. Methylene chloride product is currently loaded and transported in tank trucks, tank cars, barges and ships using open dome loading. It is also shipped in 55 gallon drums which are loaded using a flume vacuum system. Emission levels were calculated by Dow from air samples taken during tank truck and rail car loading.

Dow reported two process waste emission sources. These are a wastewater stream and spent filter elements. The two sources emit approximately 0.8 Mg/yr of methylene chloride. The wastewater stream is treated in a nonbiological treatment system, and the spent filter elements are treated in a material and energy recovery unit. The wastewater stream accounts for 99% of the secondary emissions. Dow indicated a formal wastewater monitoring procedure is followed where a sample is taken every fifteen minutes and analyzed in a gas chromatograph. Dow reported the wastewater monitoring system as a means of monitoring MC secondary emissions.

The methylene chloride emissions from 216 process equipment openings in 1983 were 0.05 Mg/yr. Ninety-five percent of the equipment openings were for pump seal replacement. The remaining five percent of equipment openings were on larger pieces of equipment during routine cleaning and inspection. Dow reported that the vessels are cleared to a concentration of 200 ppm organics before being opened. Dow did not describe the procedure followed to clear vessels of organics.

There were no emissions from process vents at the Freeport facility. Dow reported that there are no process vents and all vapor streams are recycled within the process.

Vulcan Materials - Geismar, LA[6]

Total emissions generated by the hydrochlorination process at this plant were 68.2 Mg in 1983. The largest quantity of emissions was from equipment leaks. Methylene chloride equipment leak emissions in 1983 were approximately 35.5 Mg. Product storage tanks released 19.3 Mg of methylene chloride to the atmosphere in 1983. Secondary emissions from waste treatment or disposal were 3.9 Mg. Emissions from process vents, handling, and equipment openings were 0.7 Mg/yr, 8.2 Mg/yr and 0.6 Mg/yr, respectively. Relief device discharges emitted .01 Mg of methylene chloride in 1983. All information concerning equipment (such as process vents, process components including valves and flanges, and storage facilities) and controls is considered confidential by Vulcan.

The State of Louisiana has adopted regulations for control of emissions of volatile organic compounds from storage facilities, loading facilities, process components and specific MC end uses such as surface coating and solvent metal cleaning. Methylene chloride is excluded from these regulations. However, mixed streams containing methylene chloride may be controlled under these regulations.

Vulcan Materials - Wichita, KS[7]

Emissions from MC production by the direct chlorination of methane and the hydrochlorination of methanol were 89.6 Mg at this facility in 1983. Vulcan did not distinguish equipment leaks, storage emissions, handling losses, and equipment opening losses by production process. Process vent emissions were reported only for the hydrochlorination process.

The largest quantity of emissions was from equipment leaks. Methylene chloride equipment leak emissions in 1983 were approximately 38.1 Mg. Product storage tanks released 32.2 Mg of MC to the atmosphere in 1983. Process vents emitted 12.3 Mg of MC. Emissions from handling and equipment openings were 6.2 Mg and 0.8 Mg, respectively. All information concerning equipment and controls is considered confidential by Vulcan.

There are no regulations in Kansas for control of organic compound emissions from chemical production facilities.

Diamond Shamrock - Belle, WV[8]

This plant emitted 116 Mg of MC in 1983. The largest quantity of emissions was from equipment leaks, totalling 75.2 Mg. Fifty-five percent (41.5 Mg) of the equipment leaks were from valves. Nineteen percent (14.6 Mg/yr) were from flanges and fifteen percent (11.3 Mg/yr) from pump seals. Diamond Shamrock has equipped 52 percent (13 of 25) of their pressure relief devices with rupture disks. The plant indicated that operators make hourly checks of the operating equipment to check for leaks. Also, all employees are required to wear sample pumps on their person several times per year. Exposure levels are used to identify potential problems. Since no leak repair frequency was reported by Diamond Shamrock, no control efficiency could be estimated for their inspection program and equipment leak emission estimates are for uncontrolled sources. Therefore, actual equipment leak emissions may be somewhat lower.

Emissions from sixteen fixed roof storage tanks are estimated to have been 26.1 Mg in 1983. Tanks range in volume from 250 gallons to 500,000 gallons. The 500,000 gallon fixed roof tank had 1983 emissions of 4.4 Mg and is equipped with a conservation vent, a water cooled condenser, and a freon cooled condenser for a combined estimated control efficiency of 90.7 percent. Seven other storage tanks (with volumes between 15,000 and 20,000 gallons) are equipped with conservation vents and water cooled condensers. Control efficiencies range from 41.9 percent to 86.7 percent. The remaining eight storage tanks are not equipped with emission control devices.

MC emissions from process vents were 5.7 Mg. Sixty-seven percent (3.8 Mg/yr) of these emissions were from a regeneration vent. There was no methylene chloride control device for this vent. Two vent recovery systems emitted 19 percent and 14 percent of total process vent emissions. Both vents are equipped with condensers with control efficiencies of 68.5 percent and 26.7 percent, respectively.

Total emissions from loading/handling were 4.2 Mg/yr. Methylene chloride is loaded into tank cars, tank trucks, and barges. Tank cars and tank trucks are loaded through the domes. Barges are loaded from the bottom and are vented through a four inch header on either end of the barge.

A pressure relief valve malfunction resulted in a discharge of 3.4 Mg of MC in 1983. The relief valve was on a methyl separation column reboiler. This was the only emission from relief devices in 1983.

Equipment opening losses totalled 1.1 Mg in 1983. There were 12 major equipment openings and 150 minor equipment openings.

Secondary emissions of MC from three waste streams totalled about 0.7 Mg/yr. Emissions from the waste treatment plant influent contributed only 7 percent (.05 Mg/yr) of the total. The waste is treated by steam stripping and carbon adsorption. Disposal and related activities accounted for the major portion of secondary emissions. Sixty percent (0.43 Mg/yr) of MC emissions were from drumming solid waste for off-site landfilling. Loading sludge from the waste treatment plant into bulk tank trucks for off-site treatment contributed approximately 33 percent (.24 Mg/yr) of emissions.

West Virginia does not have regulations requiring control of MC emissions from this plant.

Dow Chemical - Plaquemine, LA[9]

Dow - Plaquemine produces MC by the hydrochlorination of methanol. Total emissions of MC at the facility were 217 Mg in 1983.

The largest source of air emissions reported at the Dow facility was from loading and handling practices. Dow calculated losses to be 115 Mg (53% of total emissions). Methylene chloride is shipped by tank truck, tank car, and barge. Submerged fill pipe loading is used to reduce emissions from what would occur with splash fill loading. Louisiana regulates loading facilities for VOC with throughputs of 20,000 gallons/day or more (40,000 gallons or more for existing facilities), but methylene chloride is excluded from this regulation.

Emissions from storage facilities contributed 34 percent (73.5 Mg) of total 1983 MC emissions. Dow has five fixed roof storage tanks and one contact- internal floating roof storage tank with a mechanical shoe floating roof seal (primary only). None of the storage tanks are equipped with control devices. Louisiana regulations on VOC storage tanks are not applicable to MC.

Emissions from equipment leaks totalled 27.5 Mg in 1983. Twenty-five pressure relief devices were the largest source of emissions, releasing 8.7 Mg (32%) of the total equipment leaks emissions. One pressure relief device in gas service was equipped with a rupture disc. Emissions from valves were 8.5 Mg (31 percent) of equipment leak emissions. Nineteen percent (5.2 Mg) of the total equipment leaks emissions were released from mechanical pump seals. Liquid and gas sample connections were the sources of 15 percent of equipment leaks emissions, contributing 1.6 Mg and 2.4 Mg respectively. A compressor was the next largest source, emitting five percent (1.0 Mg) of total equipment leaks emissions. To monitor equipment for leaks, Dow has installed two process vapor phase chromatographs each capable of analyzing 10 streams. Twenty points in the process area are monitored and an alarm is set at 100 ppm. In addition, Dow requires operators to make a minimum of 12 rounds through the process, storage area per 24 hour day. Other formal division-wide programs include preventative maintenance, a pressure valve program, pressure safety valve, critical instrument, equipment thickness check, and visual internal inspections. In January, 1985 an equipment leaks emissions test conducted at Dow indicated 1.6 percent of the valves and 0.91 percent of the flanges were leaking. Calculated emission estimates incorporate this test data. Louisiana regulations requiring a VOC leak patrol/repair program do not apply to MC.

Losses from equipment openings were 0.6 Mg in 1983. The emissions were from 24 pump openings, 10 vessel openings, and 20 piping openings. Dow reported one discharge from pressure relief devices in 1983. A reactor instrument malfunction resulted in the discharge of .05 Mg of MC. A waste stream from the plant emitted approximately 0.02 Mg of MC. Dow reported no process vents emitting MC.

LCP Chemicals - Moundsville, WV[10]

The production of MC at this facility resulted in total emissions of 165 Mg MC in 1983. Emissions from two process vents were about 84.9 Mg, or 51 percent of total emissions. An unidentified process vent emitted more than 99 percent (84.3 Mg) of those emissions. LCP reported that the process vent is controlled by a chloromethanes purge condenser that is operating at 100 percent pollutant removal efficiency. However, the purge condenser is only in operation for 50 percent of the plant operating hours. Therefore, the process vent emissions reported are for when the purge condenser is inoperative and the process vent is uncontrolled. The remaining process vent emissions (.05 Mg) were from a chloromethanes recovery tank.

Emissions from equipment leaks accounted for 17 percent of total emissions, or 28.5 Mg. The largest sources of equipment leaks were valves, flanges, and pressure relief devices. Emissions from the valves were approximately 12.4 Mg (44 percent of total equipment leaks emissions). Twenty-two percent (6.2 Mg) of the emissions were from flanges. Pressure relief devices constituted 12 percent of these emissions. LCP indicated that five areas are manually sampled once per shift for contaminants. The samples are transported to the plant laboratory and analyzed by gas chromatograph. Since no leak repair frequency was reported no control efficiency could be estimated for LCPs inspection program. Therefore, all emission estimates are for uncontrolled sources. This may overstate LCP's equipment leak emissions.

Losses from product loading and handling were approximately 23.7 Mg MC in 1983. Methylene chloride is loaded into rail cars and trucks by the top splash fill method at a rate of approximately 75 gpm. Approximately 30 percent of the MC is transported by rail cars with the remaining 70 percent transported by truck.

Seven fixed roof storage tanks emitted 21.1 Mg of MC in 1983. None of the storage tanks are equipped with control devices.

Secondary emissions from three waste streams totalled 6.4 Mg in 1983. A waste stream sent to off-site treatment and disposal contributes 70 percent of the secondary emissions. Twenty-one percent of the secondary emissions were from distillation and recovery. Emissions from treatment by neutralization and carbon adsorption accounted for 9 percent of secondary emissions. LCP reported a fourth waste stream treated by neutralization. However, no information was given regarding MC concentration in this stream.

LCP reported 8 discharges from pressure relief devices in 1983. All of the discharges were due to overpressurization of a thermal reactor. Estimated emissions were 0.5 Mg.

There were 104 changeouts of liquid driers in 1983. A changeout is accomplished by opening the drier and removing the spent drier residue. LCP indicated that emissions from drier changeouts were 0.9 Mg.

West Virginia has no regulations governing volatile organic compounds.

2.4 COST OF ADDITIONAL CONTROLS

Cost estimates were developed for control of process vent, fugitive, storage, and loading emission sources not presently well controlled. The cost effectiveness to control each of these emission sources at facilities producing methylene chloride are presented in Table 2-4 and discussed in the following sections. Methods used for estimating costs are presented in Appendix B.

The achievable emission reduction for different VOC cost effectiveness ranges is presented in Table 2-5. The achievable MC emission reduction is 552 Mg. This emission reduction can be compared to total estimated MC emissions of 770 Mg in 1983 (presented in Table 2-2).

2.4.1 Control of Process Vent Emissions

Incinerator cost estimates were developed for process vents not presently controlled by 98 percent or better. These estimates along with the estimated cost effectiveness are presented in Table 2-4. Three facilities, Diamond Shamrock in Belle, WV, LCP Chemicals in Moundsville, WV, and Vulcan Chemical, in Wichita, KS reported process vents not presently controlled 98 percent or better. The cost effectiveness of controlling process vent emissions at LCP, Diamond Shamrock and Vulcan is $1,220/Mg of VOC, $16,200/Mg of VOC and $17,100/Mg of VOC respectively. The combined MC emission reduction is 88.7 Mg, an 86 percent reduction in process vent emissions from all MC production facilities.

TABLE 2-4. COST OF ADDITIONAL CONTROLS AT MC PRODUCTION FACILITIES

Company/Location	Emission Type	Control*	Control Efficiency (%)	MC/VOC Emission Reduction (Mg/yr)	Capital Cost (10^3 $)	Recovery Credit (10^3 $)	Net Annual Cost (10^3 $)	Cost Effectiveness	
								MC ($/Mg)	VOC ($/Mg)
Diamond Shamrock Belle, WV	Process	Incineration	98	5.6/25.8	1,220	0.0	418.5	74,900	16,200
	Equipment Leak	LDAR	53	40.0/81.6	58.0	33.1	29.5	737	361
	Storage	COND	85	1.1/ 1.4	111	1.0	28.1	26,100	20,700
	Storage	FR-PO	94	0.4/ 0.4	14.7	0.2	3.7	10,500	10,500
	Storage	FR-SS	97	2.8/ 2.8	16.9	2.3	2.1	753	753
	Storage	FR-SS	97	10.3/12.5	35.3	9.1	0.2	16	13
	Storage	COND	85	0.1/ 0.1	111	0.1	29.0	286,000	284,000
	Storage	COND	85	0.1/ 0.1	111	0.1	29.1	402,000	318,000
	Storage	FR-PO	94	1.8/ 1.8	32.7	0.9	7.7	4,220	4,220
	Storage	FR-SS	97	1.7/ 2.2	16.9	1.6	2.9	1,650	1,310
	Loading	COND	90	3.5/ 3.5	247	1.5	108	30,800	30,800
Dow Chemical Freeport, TX	Equipment Leak	LDAR	60	52.4/72.0	56.0	31.9	16.8	321	234
	Storage	FR-SS	97	1.9/ 1.9	19.0	1.5	3.4	1,820	1,820
	Storage	FR-SS	97	3.8/ 3.9	18.8	3.1	1.8	477	463
	Storage	FR-SS	97	3.8/ 3.9	18.8	3.1	1.8	477	463
	Loading	COND condenser	90	3.8/ 3.8	247	1.7	108	28,500	28,500
Dow Chemical Plaquemine, LA	Equipment Leak	LDAR	68	18.6/31.3	60.6	13.2	27.1	1,460	866
	Storage	FR-SS	97	6.2/ 6.2	39.1	5.0	5.2	852	852
	Storage	FR-SS	97	2.6/ 2.6	26.9	2.1	4.9	1,890	1,890
	Storage	FR-SS	97	11.7/11.7	50.6	9.5	3.8	324	324
	Storage	FR-SS	97	45.4/45.4	53.5	37.0	-22.9	-505	-505
	Loading	COND	90	51.9/51.9	247	22.8	88.1	1,700	1,700
	Loading	COND	90	51.9/51.9	380	22.8	145	2,800	2,800

(Continued)

TABLE 2-4 CONCLUDED. COST OF ADDITIONAL CONTROLS AT MC PRODUCTION FACILITIES

Company/Location	Emission Type	Control*	Control Efficiency (%)	MC/VOC Emission Reduction (Mg/yr)	Capital Cost (10^3\$)	Recovery Credit (10^3\$)	Net Annual Cost (10^3\$)	Cost Effectiveness MC (\$/Mg)	Cost Effectiveness VOC (\$/Mg)
LCP Chemicals Moundsville, WV	Process	Incineration	98	82.4/329	1,190	0.0	403	4,900	1,220
	Equipment Leak	LDAR	59	16.7/56.6	133	21.3	27.0	1,620	478
	Storage	COND	85	3.2/ 3.2	333	2.6	84.8	26,500	26,500
	Storage	FR-SS	97	4.2/ 4.2	18.4	3.4	1.4	344	344
	Storage	FR-SS	97	10.4/10.4	35.1	8.5	0.7	69	69
	Storage	COND	85	1.5/ 1.5	111	1.2	27.9	18,900	18,900
	Storage	FR-PO	94	0.5/ 0.5	12.5	0.2	3.1	6,690	6,690
	Loading	COND	90	21.3/21.3	219	9.4	88.5	4,200	4,200
Vulcan Chemical Geismar, LA	Equipment Leak	LDAR	49	17.4/33.2	27.6	13.6	20.1	1,150	605
	Storage	FR-SS	97	14.5/14.5	105	11.8	15.7	1,080	1,080
	Storage	FR-PO	94	4.2/ 4.2	77.1	2.0	18.2	4,370	4,370
	Loading	COND	90	4.0/ 4.0	83.6	1.7	166	41,400	41,400
Vulcan Chemical Wichita, KS	Process	Incineration	98	0.7/24.1	1,210	0.0	410	585,000	17,100
	Equipment Leak	LDAR	58	22.0/50.5	47.5	20.1	21.0	954	416
	Storage	COND	85	0.4/ 0.4	111	0.3	28.8	80,200	80,200
	Storage	COND	85	0.6/ 0.6	111	0.5	28.6	49,100	49,100
	Storage	COND	85	0.4/ 0.4	111	0.3	28.8	80,900	80,900
	Storage	COND	85	0.8/ 0.8	333	0.6	86.7	112,000	112,000
	Storage	COND	85	11.9/11.9	222	9.7	485	4,060	4,060
	Storage	COND	85	8.1/16.2	111	9.2	19.9	2,460	1,230
	Storage	COND	85	0.5/ 9.5	111	3.4	25.8	54,300	2,710
	Loading	COND	90	5.6/ 5.6	247	2.5	107	19,100	19,100

*Abbreviations
FR-SS: Floating roof with primary and secondary seals.
FR-PO: Floating roof with primary seals only.
COND: Refrigerated condenser.
LDAR: Leak Detection and Repair.

[a] Product storage tank: emissions previously described as process vent emissions.

TABLE 2-5. ESTIMATED MC EMISSION REDUCTIONS FOR MC PRODUCTION FACILITIES AS A FUNCTION OF COST EFFECTIVENESS

Cost Effectiveness Range ($/Mg VOC)	Nationwide MC Emission Reduction (Mg/yr)				
	Process	Equipment Leaks	Storage	Loading	Total
Credit	-	-	45.4	-	45.4
0 - 500	-	131	44.2	-	175
501 - 1000	-	36.0	9.0	-	45.0
1001 - 2000	82.4	-	28.8	51.9	163
2001 - 5000	-	-	18.1	73.2	91.3
> 5000	6.3	-	9.1	16.9	32.3
TOTAL	88.7	167	155	142	552

2.4.2 Control of Equipment Leak Emissions

The costs for additional control of equipment leak emissions from process components were estimated based on the requirements of the benzene equipment leaks NESHAP and the equipment count data supplied by the production facilities. The potential reduction in emissions from equipment leaks is estimated to be 167 Mg MC, 57 percent of total emissions from equipment leaks. Control efficiencies associated with controlling equipment leak sources range from 49 percent at the Vulcan-Geismar facility to 68 percent at the Dow-Plaquemine plant. MC emission reductions range from 16.7 Mg at the LCP plant (control efficiency 58 percent) to 52.4 Mg at Dow-Freeport (control efficiency 60 percent). The cost effectiveness of controlling equipment leaks ranges from $234/Mg VOC at Dow-Freeport to $866/Mg VOC at the Dow-Plaquemine plant.

2.4.3 Control of Storage Emissions

Cost estimates were developed for control of storage emissions from tanks not presently controlled by floating roofs, vapor recovery (85 percent control or better), or incineration. Three control options were evaluated: contact internal floating roof with primary seal only, contact internal floating roof with primary and secondary seals, and a refrigerated condenser for vapor recovery. Internal floating roofs were not costed for tanks smaller than 2 meters in diameter or horizontal tanks. Costs/cost-effectiveness estimates are presented in Table 2-4 for the most cost effective option. Using the most cost-effective option, storage emissions may be reduced by 155 Mg of MC (82 percent). The estimated cost effectiveness ranges from a net credit of $505/Mg of VOC to $573,000/Mg of VOC for the most cost-effective option on individual tanks. The estimated MC cost effectiveness is almost identical because these tanks store product MC typically greater than 99 percent pure. Since emissions are a function of throughput as well as size, there is no direct correlation between tank size and cost effectiveness. Achievable storage tank emission reduction as a function of cost effectiveness is presented in Table 2-5.

2.4.4 Control of Loading Emissions

Costs and cost-effectiveness estimates were developed for each uncontrolled land and marine loading operation. A refrigerated vapor recovery system operating at 90 percent MC removal efficiency was used as the control technique. The estimated costs of controlling each type of loading operation at individual facilities are presented in Table 2-4. The range of estimated cost effectiveness is $1,700/Mg VOC to $41,400/Mg of VOC. Using refrigerated vapor recovery as the control technique, total loading emissions may be reduced by 142 Mg (88 percent).

2.5 REFERENCES

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3.0 OTHER CHEMICAL PLANTS

3.1 PROCESS DESCRIPTIONS, EMISSIONS, AND CURRENT CONTROLS

This chapter presents the emissions and controls associated with the use of methylene chloride (MC) as a raw material used in the synthesis of other chemical products. Eleven plants use MC in production processes. These processes include: triacetate fibers, polycarbonate resin, plastics, rubber cement, rubber accelerator, insulating materials, specialty chemicals, vinyl chloride monomer, and production of BAYGON^R 1.5, a pesticide. Emissions from BAYGON^R 1.5 production are duscussed in this chapter since detailed emission estimates were received from the company for this facility. The chapter on Pesticide Manufacturing (Ch. 8) presents only generalized consumption and emissions information for the pesticide industry. MC is also used in other chemical production processes which are not identified because the company either considers production process descriptions as proprietary information, or the company did not provide sufficient information on the type of operation.

Methylene chloride emissions from these chemical plants are from equipment leaks, raw material storage, process vents, equipment openings, loading and handling, and secondary sources. The plants using MC in production and the types and amounts of emissions from these plants are presented in Table 3-1.

3.1.1 Triacetate Fiber Production

Triacetate fiber is manufactured by Celanese Fibers Operation in Rock Hill, South Carolina. Methylene chloride is used by Celanese to dissolve triacetate polymer flake and form a liquid polymer (referred to as "dope") that is suitable for extruding.

3.1.1.1 Process Description[1]. A solution of methylene chloride and methanol is fed into a batch mixer containing triacetate polymer flakes and other dry ingredients.

TABLE 3-1. TOTAL EMISSIONS FROM CHEMICAL PLANTS USING METHYLENE CHLORIDE IN PRODUCTION

Plant/Location	1983 Methylene Chloride Emissions (Mg/Yr)							
	Process	Equipment Leaks[a]	Relief Devices	Storage[b]	Handling	Equipment Openings	Secondary	Total
B.F. Goodrich, Plant I Cleveland, OH	65.6[c]	4.6	---	0.2	---	---	169	239
B.F. Goodrich, Plant II Cleveland, OH	7.5	10.1	---	0.5	---	---	---	18.1
Borden Chemical Fremont, CA	2.2	0.003	---	---	---	---	0.3	2.5
Borden Chemical Norristown, PA	---	2.1	---	0.8	0.3	---	---	3.2
Celanese Rock Hill, SC	5150	22.0	2.7	---	0.5	---	---	5180
Dow Chemical Midland, MI	1120	207	0.1	29.0	2.7	4.3	88.5	1450
General Electric Mount Vernon, IN	2680	247	---	---	---	63.7	584	3570
General Electric Pittsfield, MA	64.9	6.1	---	0.3	0.2	2.3	0.2	74.0
General Electric Schenectady, NY	0.01	0.001	---	---	---	---	0.2	0.2
Mobay Chemicals Baytown, TX	0.4	51.2	---	0.2	0.6	16.5	74.4	143
Mobay Chemicals Kansas City, MO	---	0.02	---	0.4	---	---	---	0.4
Shell Deer Park, TX	---	---	---	---	---	---	0.06	0.06
	9090	550	2.8	31.0	4.3	86.8	917	10,700

[a] Based on equipment count provided by plants and SOCMI fugitive emission factors.

[b] Based on storage tank information provided by plants and AP-42 equations.

[c] Combined emissions from process vents, equipment openings, and loading and handling.

The solvents are slowly mixed with the solids until the solids are completely dissolved, forming the liquid polymer dope. The dope is then filtered and pumped to the extrusion area, where it is preheated, and then extruded and dried. The dried fibers are spun onto bobbins until further processing including twisting, coning, and beaming. A process flow diagram is shown in Figure 3-1.

3.1.1.2 Current Emissions and Controls[2]. Methylene chloride emissions totalled 5180 Mg at the Celanese facility in 1983. Emission sources, current controls, control efficiencies, and emission amounts are given in Table 3-2. The major emission source from triacetate fiber production is from solvent recovery. Carbon adsorption units operating at a reported control efficiency of greater than 98 percent are used to recover spent solvent. Emissions from the units were 5150 Mg in 1983. Celanese did not report any other process vent emission points.

Equipment leaks were the source of 22.0 Mg of MC emissions. Valves contributed 51 percent (11.2 Mg) of those emissions. Flanges and pumps seals emitted 22 percent (4.9 Mg) and 21 percent (4.6 Mg), respectively. To monitor for equipment leaks, Celanese operates four infra-red gas analyzers in different process areas. The analyzers measure room concentrations and are equipped with recorders and alarms. These instruments are useful in detecting process upsets and spills, but not for determining individual equipment leaks. Celanese did not report a leak repair program, therefore no control efficiency could be estimated for their inspection program and emission estimates are for uncontrolled sources. This may overstate somewhat Celanese's equipment leak emissions.

Handling emissions accounted for about 0.5 Mg of MC emissions at the Celanese facility. Methylene chloride is received by tank truck and tank car. The tank truck or tank car compartments are pressurized with inert gas and the MC is pumped to storage tanks. The storage tanks are tied into the solvent recovery ducting. Therefore, losses occur only when the tank truck or car is empty and the compartment is depressurized into the atmosphere. Celanese indicated that there are no emissions from MC storage since storage tanks are vented into the solvent recovery ducting.

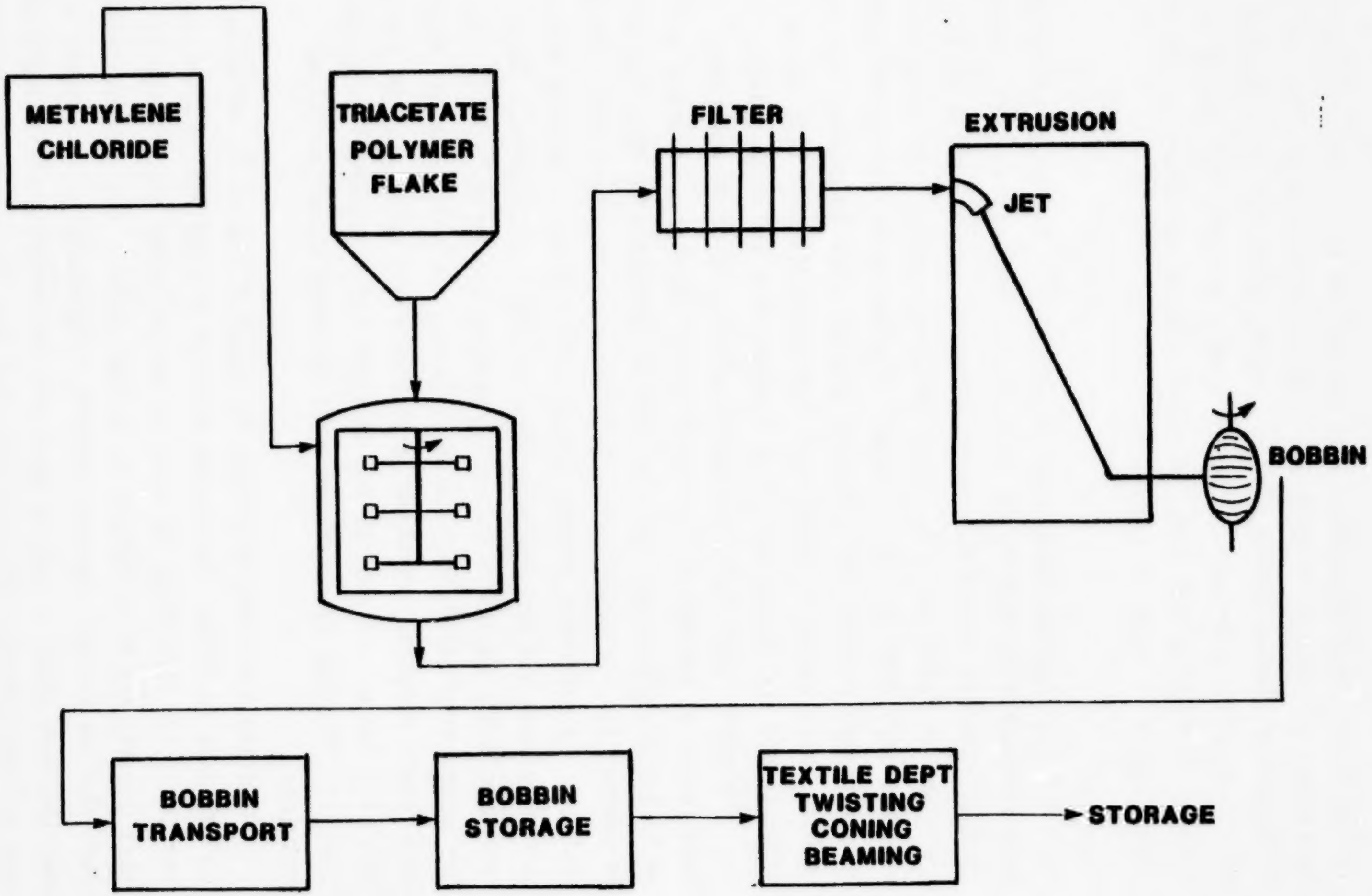
METHYLENE CHLORIDE
TRIACETATE POLYMER FLAKE
FILTER
EXTRUSION
JET
BOBBIN
BOBBIN TRANSPORT
BOBBIN STORAGE
TEXTILE DEPT TWISTING CONING BEAMING
STORAGE

Figure 3-1. Process flow diagram for the production of triacetate fiber.

TABLE 3-2 ESTIMATED EMISSIONS AND CURRENT CONTROLS AT FACILITIES USING METHYLENE CHLORIDE IN PRODUCTION

Company/Location	Product	Type of Emissions	Present Controls	Reported Control Efficiency (%)	Present MC Emissions (Mg/yr)	Comments
B.F. Goodrich Cleveland, OH Plant I	Rubber Accelerator	Miscellaneous[a]			65.6	From mass balance-See discussion
		Equipment Leaks	None	0	4.6	Visual inspection
		Storage o Fixed-Roof Tank	None	0	0.2	
		Secondary o Product water wash	To POTW	NR	169	
B.F. Goodrich Cleveland, OH Plant II	Rubber Accelerator	Process o Vacuum jet pump	Water cooled condenser, refrigerated condenser	94	7.5	
		Equipment Leaks	None	0	10.1	No monitoring
		Storage o Pressure vessel	Back pressure relief valve	NR	0.06	750 gallons
		o Pressure vessel	Back pressure relief valve	NR	0.1	750 gallons
		o Pressure vessel	Back pressure relief valve	NR	0.4	750 gallons
Borden Chemical Fremont, CA	Rubber Cement	Process o Adhesives fume collection	None		2.2	
		Equipment Leaks	None	0	0.003	4 process components
		Secondary o Waste product drums	To solvent reclaimer	NR	0.3	
Borden Chemical Norristown, PA	Liquid Chemical Specialty Products	Equipment Leaks	None	0	2.1	Visual inspection
		Storage o Fixed-Roof Tank	None	0	0.4	5,000 gallons
		o Fixed-Roof Tank	None	0	0.2	10,000 gallons
		o Fixed-Roof Tank	None	0	0.1	5,000 gallons
		o Fixed-Roof Tank	None	0	0.06	3,000 gallons

(Continued)

TABLE 3-2 CONTINUED. ESTIMATED EMISSIONS AND CURRENT CONTROLS AT FACILITIES USING METHYLENE CHLORIDE IN PRODUCTION

Company/Location	Product	Type of Emissions	Present Controls	Reported Control Efficiency (%)	Present MC Emissions (Mg/yr)	Comments
Borden Chemical Norristown, PA (Cont'd)		Handling o Tank trucks o Product handling	None	0	0.3	
Celanese Rock Hill, SC	Triacetate Fibers	Process o Solvent Recovery	Carbon Adsorption	98^b	5150	
		Equipment Leaks	Infra-red gas analyzers	0	22.0	
		Handling o Tank truck, tank car	Vent to solvent recovery	NR	0.5	
		Relief Devices	NA		2.7	Mixer Rupture Disharge
Dow Chemical (#5) Midland, MI	Unidentified	Process o *	*	*	1.7	3 vents
		Equipment Leaks	Pressure relief device controls	0	8.2	Visual inspection preventive maintenance
		Storage o Fixed-Roof Tank	Vapor Return Conservation vent	98^b	0.003	
		Equipment opening	None	0	0.02	17 openings
		Handling o Tank truck	Vapor balance line	95	0.03	
Dow Chemical (#6) Midland, MI	Unidentified	Process o *	*	*	67.1	1 vent
		Equipment Leaks	Pressure relief device controls	0	16.6	Visual inspection preventive maintenance
		Storage o Pressure vessel	None	0	.01	30 gallons
		o Pressure vessel	None	0	.02	100 gallons
		Equipment opening	None	0	0.04	200 openings (Experimental process-small lines)

(Continued)

TABLE 3-2 CONTINUED. ESTIMATED EMISSIONS AND CURRENT CONTROLS AT FACILITIES USING METHYLENE CHLORIDE IN PRODUCTION

Company/Location	Product	Type of Emissions	Present Controls	Reported Control Efficiency (%)	Present MC Emissions (Mg/yr)	Comments
Dow Chemical (#7) Midland, MI	Unidentified	Process				
		o *	*	*	54.5	1 vent
		Equipment Leaks	None	0	5.5	Visual inspection preventive maintenance
		Equipment opening	None	0	0.2	2 openings
		Secondary				
		o Liquid waste stream	Biological Treatment	NR	40.2	
Dow Chemical (#8) Midland, MI	Unidentified	Process				
		o *	*	*	52.5	4 vents
		Equipment Leaks	Chromatographic Air Monitoring Pressure Relief device controls	NR	60.1	
		Equipment opening	None	0	0.3	54 openings
		Secondary				
		o Liquid waste stream	Biotreatment	NR	0.006	
		o Liquid waste stream	Biotreatment	NR	1.0	
		o Liquid waste stream	Process Recovery	NR	12.8	
		o Liquid waste stream	Process Recovery	NR	0.01	
		o Liquid waste stream	Incinerator	NR	0	
Dow Chemical (#9) Midland, MI	Unidentified	Process				
		o *	*	*	135	2 vents
		Equipment Leaks	Pressure relief device controls		13.3	Visual inspection Preventive maintenance
		Storage				
		o Pressure vessel	Pressure Relief Device	NR	0.5	10,000 gallons
		o Pressure vessel	Pressure Relief Device	NR	0.1	500 gallons
		o Pressure vessel	Pressure Relief Device	NR	1.0	8,000 gallons
		Handling				
		o Tank cars	None	0	1.4	

(Continued)

TABLE 3-2 CONTINUED. ESTIMATED EMISSIONS AND CURRENT CONTROLS AT FACILITIES USING METHYLENE CHLORIDE IN PRODUCTION

Company/Location	Product	Type of Emissions	Present Controls	Reported Control Efficiency (%)	Present MC Emissions (Mg/yr)	Comments
Dow Chemical (#10) Midland, MI	Unidentified	Process				
		o *	*	*	0.7	2 vents
		Equipment Leaks	Quarterly air monitoring pressure relief device controls	NR	27.6	Visual inspection
		Storage				
		o Pressure vessel	None	0	1.0	32,000 gallons
		Equipment openings	None	0	0.7	100 openings
		Handling				
		o Rail car	None	0	1.3	
		Secondary				
		o Liquid Waste Stream	Biotreatment	NR	1.2	
Dow Chemical (#11) Midland, MI	Unidentified	Equipment Leaks	Continuous Air Monitor	NR	6.7	20 sampling probes
		Storage				
		o Fixed-Roof Tank	Relief Valve	NR	0.4	2,850 gallons
		o Fixed-Roof Tank	Relief Valve	NR	0.4	2,850 gallons
		o Fixed-Roof Tank	Relief Valve	NR	0.08	1,900 gallons
		o Fixed-Roof Tank	Relief Valve	NR	0.08	2,000 gallons
		o Fixed-Roof Tank	Relief Valve	NR	0.02	2,850 gallons
		Equipment opening	None	0	0.5	115 openings
Dow Chemical (#12) Midland, MI	Unidentified	Process				
		o *	*	*	810.8	3 vents
		Equipment Leaks	Continuous Air Monitor	NR	68.7	20 sampling probes
		Storage				
		o Fixed-Roof Tank	Relief Valve	NR	12.0	47,000 gallons
		o Fixed-Roof Tank	Vented to Scrubber	NR	3.7	5,900 gallons
		o Pressure vessel	Water seal and relief valve	NR	4.7	12,900 gallons
		o Fixed-Roof Tank	Vented to Scrubber	NR	1.8	5,900 gallons
		o Fixed-Roof Tank	Vented to Scrubber	NR	1.9	4,300 gallons
		o Fixed-Roof Tank	None	0	1.0	12,900 gallons
		Equipment opening	None	0	2.5	234 openings
		Secondary				
		o Liquid waste stream	Biological Treatment	5	33.3	
		Relief devices	NA		0.1	Storage tank corrosion failure

(Continued)

TABLE 3-2 CONTINUED. ESTIMATED EMISSIONS AND CURRENT CONTROLS AT FACILITIES USING METHYLENE CHLORIDE IN PRODUCTION

Company/Location	Product	Type of Emissions	Present Controls	Reported Control Efficiency (%)	Present MC Emissions (Mg/yr)	Comments
General Electric Mount Vernon, IN	Polycarbonate Resin	Process				
		o Hopper Dryers	None	0	17.0	41 dryers
		o Hopper Dryers	None	0	18.6	45 dryers
		o Extruder Die Hoods	None	0	224.6	7 hoods
		o Extruder Die Hood	None	0	4.5	1 hood
		o Extruder Die Hood	None	0	2.5	1 hood
		o Extruder Die Hood	None	0	8.8	1 hood
		o Extruder Die Hood	None	0	13.4	1 hood
		o Extruder Die Hood	None	0	0.2	1 hood
		o Molding Machine Vents	None	0	4.8	2 vents
		o Q.A. Hood Vent	None	0	6.4	4 vents
		o Extruder Die Vents	None	0	391	17 vents
		o Extruder Vacuum Pump	None	0	86.4	6 pumps
		o Extruder/Die Vent	None	0	11.2	3 vents
		o Extruder/Die Vent	None	0	93.8	8 vents
		o Molding Machine	None	0	3.2	2 units
		o Vacuum Stripping Blowers	None	0	0.6	4 units
		o Vent Gas Absorber	Water Scrubber	87	477.3	1 vent
		o Vent Gas Absorber	Water Scrubber	87	477.3	1 vent
		o Carbon Adsorption System	Carbon Bed	87	46.2	
		o Filter Receiver	None	0	85.6	2 units
		o Filter Receiver	None	0	85.6	2 units
		o Weight Hopper Vent	None	0	0.6	2 units
		o Feed Hopper	None	0	0.3	1 unit
		o Surge Hopper	None	0	7.6	2 units
		o MC Storage Tank	Conservation Vent	10	17.6	
		o Storage Silo	None	0	170	
		o Solvent Recovery	Carbon Bed	87	347	
		o MC Dryer System	Knock Out Pot/Demister	50	79.6	
		o Tar/Isomer Storage	None	0	0.4	
		Equipment Leaks				
		o Building 14/16	Photo ionization detection system	0	175	Monitors 40 points
		o Building 15/31	Photo ionization detection system	0	71.8	Monitors 10 points

(Continued)

TABLE 3-2 CONTINUED. ESTIMATED EMISSIONS AND CURRENT CONTROLS AT FACILITIES USING METHYLENE CHLORIDE IN PRODUCTION

Company/Location	Product	Type of Emissions	Present Controls	Reported Control Efficiency (%)	Present MC Emissions (Mg/yr)	Comments
General Electric Mount Vernon, IN (Cont'd)		Storage				
		o 44 process and storage vessels	Vent gas absorbers	87	0.1	Bldg 14/16
		o Pressure Vessel	Conservation Vent	10	1.5	Bldg 15/31
		Equipment Opening	None	0	63.7	
		Secondary				
		o Biological Treatment	None	0	584	
General Electric Pittsfield, MA	Plastics Manufacture	Process				
		o Reactor Vent	None	0	4.6	
		o Phosgonation Reactor	None	0	2.4	
		o Precip.Room Vent	None	0	1.8	
		o Work-up Room Vent	None	0	1.3	
		o Stripper Room Vent	None	0	1.8	
		o Stripper Room Vent	None	0	1.8	
		o Percip. Condenser Vent	Condenser	50	27.2	
		o MC Still Watertank	None	0	0.9	
		o Area Vent	None	0	2.7	
		o MC Still Vent	Condenser	97	8.2	
		o MC/Water Separator	None	0	1.8	
		o Still Decant Tank	None	0	0.5	
		o Dryer Vacuum Pump	Condenser	50	9.8	
		Equipment leaks	None	0	6.1	Leaks detected by observation and weekly mass balance
		Storage				
		o Fixed-Roof Tank	To Condenser	50	0.09	4100 gallons
		o Fixed-Roof Tank	None	0	0.06	500 gallons
		o Fixed-Roof Tank	None	0	0.06	500 gallons
		o Fixed-Roof Tank	To Condenser	50	0.007	1500 gallons
		o Fixed-Roof Tank	To Condenser	50	0.1	1250 gallons
		o Fixed-Roof Tank	None	0	0.005	250 gallons

(Continued)

TABLE 3-2 CONTINUED. ESTIMATED EMISSIONS AND CURRENT CONTROLS AT FACILITIES USING METHYLENE CHLORIDE IN PRODUCTION

Company/Location	Product	Type of Emissions	Present Controls	Reported Control Efficiency (%)	Present MC Emissions (Mg/yr)	Comments
General Electric Pittsfield, MA (Cont'd)		Equipment Opening	None	0	2.3	2000 openings
		Handling				
		o Drums	None	0	0.2	Present delivery via tank trucks.
		Secondary				
		o Aqueous waste stream	To Sewage Treatment	80	0.1	
		o Drums	To Haz.Waste Disposal	98^b	0.01	
General Electric Schenectady, NY	Insulating Materials	Process				
		o *	*	*	0.01	
		Secondary				
		o *	*	*	0.2	
Mobay Chemicals Baytown, TX	Polycarbonate Resin	Process				
		o Vent	Scrubber	98	0.3	
		o Reactor Vent	None	0	0.07	
		o Reactor Vent	None	0	0.05	
		Equipment Leaks	Monthly Portable Gas Chromatograph Check, Pressure Relief Device Controls	NR	51.2	
		Equipment opening	None	0	16.5	Primarily sampling openings
		Storage				
		o Fixed-Roof Tank	Vent to Scrubber	98	0.006	27,100 gallons
		o Fixed-Roof Tank	Vent to Scrubber	98	0.006	150,000 gallons
		o Fixed-Roof Tank	Vent to Scrubber	98	0.1	85,200 gallons
		o Fixed-Roof Tank	Vent to Scrubber	98	0.1	85,200 gallons
		o Fixed-Roof Tank	Vent to Scrubber	98	0.003	27,100 gallons
		Secondary				
		o Wastewater stream	Biological & Carbon Treatment	NR	22.0	
		o Contained solvent	Incineration	NR	0	
		o Process Water Trench	Biological & Carbon Treatment	80	11.0	
		o Leaks and spills	None	0	41.4	

(Continued)

TABLE 3-2 CONCLUDED. ESTIMATED EMISSIONS AND CURRENT CONTROLS AT FACILITIES USING METHYLENE CHLORIDE IN PRODUCTION

Company/Location	Product	Type of Emissions	Present Controls	Reported Control Efficiency (%)	Present MC Emissions (Mg/yr)	Comments
Mobay Chemicals Kansas City, MO	BAYGON 1.5	Handling o Rail car, tank truck	None	0	0.6	
		Equipment Leaks	None	0	0.02	No monitoring
		Storage o Fixed-Roof Tank	None	0	0.4	No longer uses on-site storage
Shell Deer Park, TX	Vinyl Chloride Monomer	Secondary o Waste stream one	Biotreatment	NR	0.06	

*The company considers this confidential information.

[a] Combined emissions from process vents, equipment openings, and loading and handling.

[b] Company reported greater than 98 percent control, but only 98 percent is accepted without supporting test data.

NR = Not reported.
NA = Not applicable.

Celanese reported one discharge from a pressure relief device on a mixer. The discharge resulted in 2.7 Mg of MC emissions.

South Carolina has developed regulations pertaining to emissions of volatile organic compounds (VOC) from specific sources, such as solvent metal cleaning and storage tanks. However, methylene chloride is excluded from these regulations in South Carolina due to its negligible photochemical reactivity.

3.1.2 Polycarbonate Resin

Polycarbonate resins were manufactured by two producers in 1983. These are General Electric in Mount Vernon, Indiana, and Mobay Chemical in Baytown, Texas. Methylene chloride is used by both plants as a solvent in the polymerization reaction.

3.1.2.1 Process Description[1]. Bisphenol-A is reacted with phosgene in the presence of pyridine to form a polycarbonate. MC is used as a solvent in the polymerization reaction. The reaction is carried out at a temperature below 40°C (104°F) with a residence time of 1 to 3 hours. The polycarbonate production process occurs according to the reaction:

$$\underset{\text{(Bisphenol-A)}}{HO_6H_4C(CH_3)_2C_6H_4H} + \underset{\text{(phosgene)}}{COCl_2} \xrightarrow[\text{MC}]{\text{pyridine}} \text{polycarbonate resin}$$

Following reaction, reactor contents are washed to remove excess pyridine from the polymer/methylene chloride stream. This stream is treated with an organic compound, such as aliphatic hydrocarbon, to effect precipitation of the polymer. After the polycarbonate precipitates, it is filtered and dried. Methylene chloride is present in all process steps. A process flow diagram is shown in Figure 3-2.

3.1.2.2 Current Controls and Emissions. The types of emissions from this process at the two production facilities are from process vents, equipment leaks, storage, handling, equipment openings, and secondary sources. The emission types and their controls are discussed below.

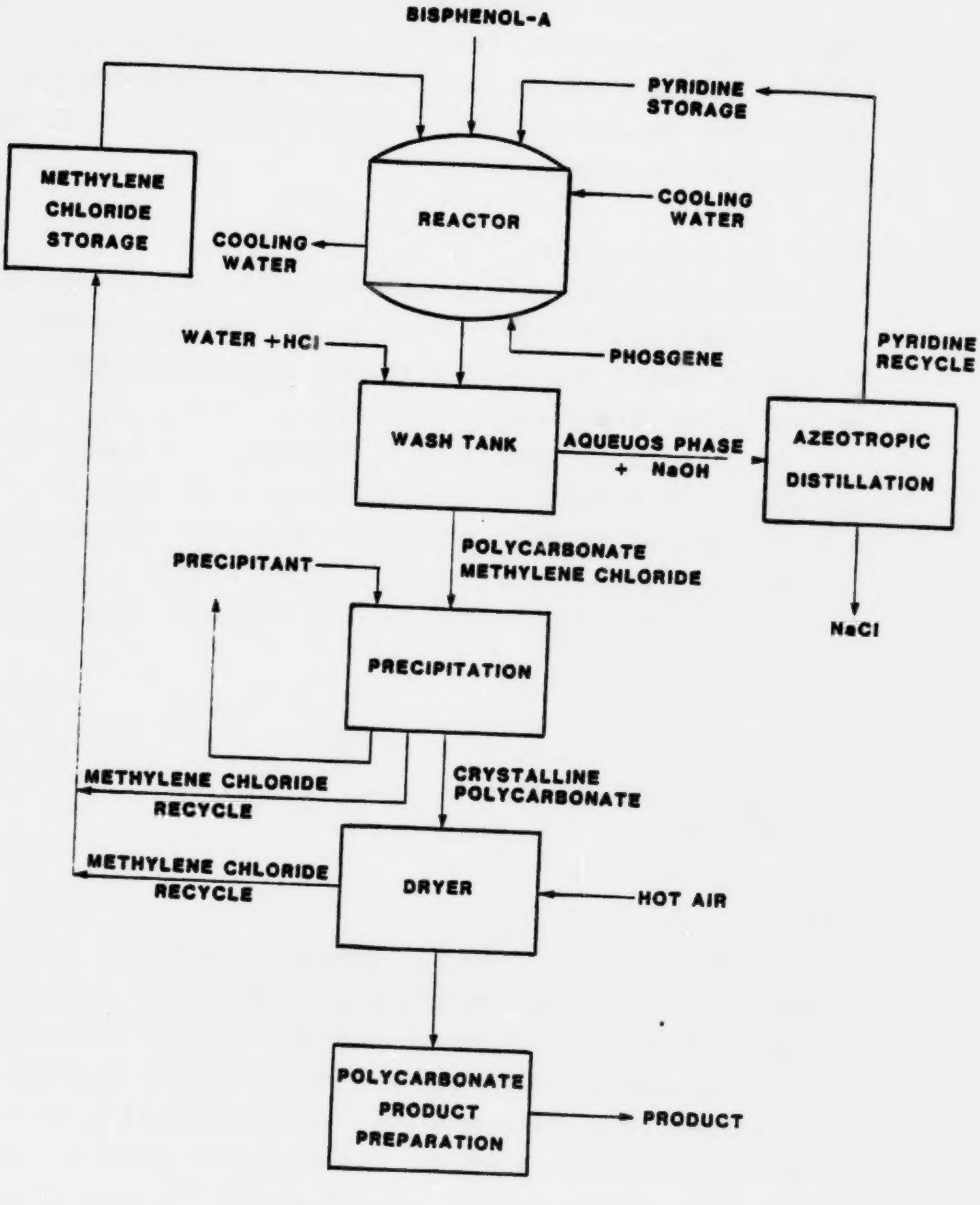
BISPHENOL-A
PYRIDINE STORAGE
METHYLENE CHLORIDE STORAGE
REACTOR
COOLING WATER
COOLING WATER
WATER +HCl
PHOSGENE
PYRIDINE RECYCLE
WASH TANK
AQUEUOS PHASE + NaOH
AZEOTROPIC DISTILLATION
PRECIPITANT
POLYCARBONATE METHYLENE CHLORIDE
NaCl
PRECIPITATION
METHYLENE CHLORIDE RECYCLE
CRYSTALLINE POLYCARBONATE
METHYLENE CHLORIDE RECYCLE
DRYER
HOT AIR
POLYCARBONATE PRODUCT PREPARATION
PRODUCT

Figure 3-2. Process flow diagram for the Production of polycarbonate resin.

General Electric - Mount Vernon, Indiana

The production of polycarbonate resins and proprietary associated processes at this facility resulted in 3,570 Mg of MC emissions in 1983. General Electric indicated that emissions reported for individual sources were either rough estimates or maximum allowable permitted levels and that they could not give exact values for each emission source. Actual emissions in 1983 were much lower than the reported levels. General Electric reported 4 process areas emitting MC. Two of the process areas use methylene chloride in polycarbonate synthesis. Therefore emissions result from process vents as well as equipment leaks and equipment openings. The other two areas are used in polycarbonate processing and MC emissions result from residual in materials processed. Emission sources, current controls, control efficiencies, and emission quantities are presented in Table 3-2. Process vents were the source of 2,680 Mg of those emissions. Seventeen extruder die vents emitted about 391 Mg MC (27 percent of total process vent emissions). Seven extruder die hoods emitted approximately 225 Mg MC (15 percent of process vent emissions). Neither the extruder die vents nor the extruder die hoods are equipped with MC control devices. Other major uncontrolled contributors include six extruder vacuum pumps 86.4 Mg/year emissions), eight more extruder die vents (93.8 Mg/year emissions), two filter receivers emitting 85.6 Mg of MC each, and two storage silos emitting 85.0 Mg of MC each.

General Electric reported control devices on 6 process vents. Two vent gas absorbers are controlled by water scrubbers at an estimated 87 percent MC control efficiency. Emissions from the vent gas absorbers were 477 Mg each. Two carbon adsorbers control various process vents. The adsorbers achieve 87 percent pollutant removal giving final emission levels of 46.3 Mg and 348 Mg. A MC dryer system is equipped with a knock-out Pot/Demister that reduced emissions by 50 percent, to 79.5 Mg. General Electric also reported a conservation vent on a MC storage tank with 10 percent control efficiency. The storage tank emissions were 17.6 Mg of MC. This tank was reported as a process vent by General Electric.

Current estimates for emissions from secondary sources are 584 Mg/year. General Electric estimates that approximately 1,818 kg/day MC is discharged to the site sewer system. Approximately 218 kg/day reaches the wastewater treatment plant for on-site biological treatment. The remaining 1,600 kg/day is lost to the atmosphere in three areas: (1) the Brine Recovery Operation,(2) the sewer system, and (3) the wastewater treatment plant prior to biological treatment.

Equipment leaks were the next largest source of emissions generated at the General Electric facility, totalling 247 Mg of MC. General Electric reported equipment counts for two of four process areas. The other two process areas do not have equipment in MC service and emissions result from residual in materials processed. Equipment leaks in one process building resulted in emissions of 176 Mg MC with flanges being the major contributor (42 percent). General Electric reported that multipoint programmable sequence area monitoring is performed to detect MC leaks using a photo ionization detection HNu system. Forty points are monitored throughout the process area. According to General Electric, the monitoring has proven effective in identifying major leak occurrences and the instrumentation can detect MC in the low ppm range. However, sample system limitations with 40 sample points can inhibit detection of minor leaks and spillage. No information was reported about the frequency of repair of leaks. Therefore, uncontrolled emission factors were used to estimate equipment leak emissions, possibly resulting in an overestimate of these emissions. Equipment opening losses in this process area were reported as 5.1 Mg in 1983. The number of equipment openings was not provided, but this emissions estimate was based on scheduled maintenance activities assuming 100 percent loss of estimated quantities in the system at the time of opening.

Equipment leak losses in a second process building totalled 71 Mg MC. General Electric also utilizes a HNu system in and around the primary potential leak areas in this building. Continuous area monitoring is performed at 10 points in the operation. General Electric did not report the frequency of leak repair for this area. Therefore, uncontrolled emission factors were used to estimate equipment leak emissions and these emission levels may be overstated.

Equipment opening losses in this area were 58.6 Mg, as a result of weekly recorded activities for several hundred pieces of equipment. General Electric based this emission figure on field estimates of quantities in the system at the time of opening, and extrapolated emissions out using 100 percent loss and number of occurrences.

There are 45 process and storage vessels for MC at this facility. All but one of these vessels vent to gas absorbers, with an estimated 87 percent control efficiency. The remaining vessel is equipped with a conservation vent with an estimated 10 percent control efficiency. Emissions from storage facilities were 1.6 Mg in 1983.

Indiana has adopted regulations limiting the allowable emissions of volatile organic compounds to 100 tons per year or an 85 percent reduction of emissions. However, the regulations exclude non-photochemically reactive hydrocarbons and organic compounds that are not liquid at standard conditions. Methylene chloride is excluded from these regulations due to its negligible photochemical reactivity.

Mobay Chemical - Baytown, Texas[4]

The polycarbonate resin process generated 143 Mg MC emissions at this facility in 1983. Table 3-2 documents emission sources, current controls, control efficiencies, and emission amounts for this facility.

Emissions from secondary sources were the largest source of MC emitters at 74.4 Mg. Mobay listed three sources for these emissions: 1) a wastewater stream going to biological and carbon treatment (22.1 Mg), 2) a process water trench also going to biological and carbon treatment (10.9 Mg), and 3) other leaks and losses prior to maintenance work (41.4 Mg).

Emissions from equipment leaks were 51.2 Mg in 1983. Valves emitted 55 percent (28.4 Mg). Flanges accounted for 19 percent (9.5 Mg) and pump seals emitted 15 percent (7.6 Mg). Mobay has 33 pressure relief devices protected by rupture disks. Twenty more relief valves are vented to a scrubber to control emissions. Five pressure relief valves are unprotected.

Mobay records process variables each shift to detect obvious leaks. Also, a daily walkthrough is performed to spot leaks. A solvent inventory is taken each week to account for any unusual loss. All pump seals and vent locations are checked monthly with a portable gas chromatograph. In addition, one technician devotes half-time to solvent loss prevention. Mobay believes this monitoring system is reasonably effective for obvious losses. Mobay did not report the frequency of leak repairs and emissions from equipment leaks were calculated using uncontrolled emission factors. Therefore, these emissions may be overstated.

Losses from equipment openings were 16.5 Mg in 1983. Forty-four percent (7.3 Mg) of equipment openings losses were due to daily sampling. Mobay reports that approximately 50 samples are taken a day. Filter replacement contributed about 6.1 Mg (37 percent) of MC emissions. Replacement of an 80,000 gallon product tank emitted 1.6 Mg. Other equipment opening losses were due to routine maintenance of purification equipment, pump seal replacement, heat exchanger replacement, and from opening open solvent lines to remove pluggage.

Solvent handling losses were 0.6 Mg. MC is delivered by rail car and/or tank truck. No control equipment is used to reduce emissions during unloading.

Emissions from three process vents totalled 0.4 Mg in 1983. A process vent scrubber operating at 98 percent MC removal efficiency emits 0.3 Mg MC. The emission level was determined from inlet and outlet sampling and gas chromatograph analysis of the samples for composition. Two reactor vents that emit MC only when the reactor is being filled have a combined annual loss rate of about 0.1 Mg/year. Emissions occur from these vents for only about 10 minutes per month.

Losses from five fixed roof storage tanks were about 0.2 Mg in 1983. All storage tank conservation vents are vented to a scrubber. Mobay reported that sampling indicated that this control technique reduces emissions by 98 percent.

Texas has adopted regulations to control emissions from volatile organic compounds. However, methylene chloride is excluded from these regulations due to its negligible photochemical reactivity.

3.1.3 Rubber Cement Manufacturing

Methylene chloride is used in the production of rubber cement at Borden Chemical, Fremont, California. Borden considers process description information confidential.

3.1.3.1 Current Emissions and Controls. Emissions from rubber cement manufacturing at this facility are primarily from process vents, and secondary sources. In addition, some emissions result from equipment leaks. Emission levels and controls at these facilities are discussed below and are presented in Table 3-2.

The estimated methylene chloride emissions from this plant are 2.5 Mg/year. Emissions are from a process vent, waste product disposal, and equipment leaks. There were no relief device discharges or equipment openings during 1983. Methylene chloride and product containing MC are handled and stored in 5-gallon pails and 55-gallon drums. Emissions were estimated by the plant to be negligible from these sources.

An adhesives fume collection system was the primary emission source at the Borden facility with about 2.2 Mg MC emissions (Borden estimated this figure from 1984 production). MC emissions occur intermittently during the 6-hour batch cycle as the mixer lid is opened to add batch ingredients and to take product samples. The ventilation system serving the rubber cement mixers also serves several other mixers not using MC. The combined flow from all mixers discharges through one stack.

Waste product is packed in drums and sent to a solvent reclaimer for solvent recovery and/or disposal. Emissions during packing are estimated to be 0.3 Mg/year.

Equipment leaks from process components in MC service were 3 kg (.003 Mg) in 1983. Borden has only four components in MC service, used less than 0.1 percent of the time. They have no monitoring or repair program for equipment leaks.

Fremont is in the Bay Area Air Quality Management District (BAAQMD). The BAAQMD has adopted a series of rules for the regulation of precursor organic compounds. However, in the BAAQMD, methylene chloride is defined as a non-precursor organic compound and is therefore excluded from regulation.

3.1.4 Rubber Accelerator Manufacturing

B.F. Goodrich uses MC in the production of rubber accelerator at two plants in Cleveland, Ohio. Rubber accelerator is a compound that greatly reduces the time required for vulcanization of natural and synthetic rubbers, while improving the aging and other physical properties at the same time.

3.1.4.1 Current Emissions and Controls. Emission sources from rubber accelerator manufacture at the two B.F. Goodrich plants are process vents, equipment leaks, storage, and secondary sources. Emission levels and controls at these facilities are discussed below and are presented in Table 3-2.

B.F. Goodrich - Cleveland, Ohio; Plant I[6]

B.F. Goodrich did not supply emission estimates for process vents, equipment openings, or loading and handling losses at this facility. However, a material balance was provided indicating that 70.4 Mg MC are emitted directly to the air. This figure does not include a product water wash stream containing MC that is discharged to an industrial sewer for pretreatment, and then to a publicly owned treatment works (POTW) facility. This secondary source emits 169 Mg MC. B.F. Goodrich did not indicate what fraction of MC is emitted in pretreatment prior to discharge to the POTW facility. Therefore, it was assumed all MC is emitted at the B.F. Goodrich facility.

Emission estimates were calculated for equipment leaks for process components in MC service and for storage facilities. Equipment leaks resulted in MC emissions of 4.6 Mg in 1983. Valves were the largest source of equipment leak emissions emitting 2.4 Mg MC. Sample connections were the next largest contributor with 1.1 Mg MC. Pressure relief devices emitted 0.5 Mg. B.F. Goodrich reported that process components are monitored for leaks through routine visual inspection and equipment maintenance. Since a leak repair program was not reported, emissions from equipment leaks were calculated using uncontrolled emission factors.

One fixed roof underground storage tank was the source of 0.2 Mg of MC emissions. The tank is not equipped with a control device. B.F. Goodrich reported no other storage tanks in MC service.

Equipment leaks and storage tanks result in total MC emissions of 4.8 Mg. From the material balance, if 70.4 Mg MC are emitted directly to the air, then the remaining 65.6 Mg may be assumed to be from process vents, equipment openings and loading and handling losses. B.F. Goodrich reported six process vent emission points. Four of those emission points were equipped with brine cooled shell and tube condensers operating at more than 98 percent MC removal efficiency. The remaining two process vents, a wash tank and a centrifuge blower were uncontrolled.

There were seven equipment openings at this facility in 1983. No estimate can be made on specific emission levels from these openings since B.F. Goodrich gave no indication of solvent purging procedures prior to opening. No estimate can be made on loading and handling emissions either, since no information was given on loading and handling techniques (i.e., splashfill versus dip pipe loading).

The State of Ohio has adopted regulations controlling photochemically reactive materials, hydrocarbons, and related materials. However, MC is excluded from these regulations due to its negligible photochemical reactivity.

B.F. Goodrich - Cleveland, Ohio; Plant II[6]

Emissions from process vents, equipment leaks, and storage facilities are approximately 18.1 Mg/year at this facility. The rubber accelerator manufacturing process was not in operation in 1983, so this emission level represents current conditions. However, the MC emissions were incorporated in the 1983 total MC emission estimates. Emission sources, current controls, control efficiencies, and emission quantities are reported in Table 3-2. B.F. Goodrich did not supply information concerning emissions from pressure relief devices and equipment openings.

Equipment leaks from process components are the largest source of MC emissions at 10.1 Mg/year. Valves emit 4.3 Mg (43 percent), pump seals emit 3.0 Mg (30 percent), and pressure relief devices emit 1.6 Mg. Sample connections are also minor contributors. B.F. Goodrich does not have a formal process component leak monitoring and repair program.

A vacuum jet/pump is the only process vent emitting MC. The emission rate for this vent is 7.5 Mg/year following control by a water cooled condenser and a refrigerated condenser operating at -9°C (16°F). The estimated MC removal efficiency is 94 percent.

B.F. Goodrich stores MC in three pressure vessels ranging in volume from 750 gallons to 2,000 gallons. Emissions from these storage vessels are approximately 0.5 Mg/year. These tanks are N_2 blanketed. During filling operations, the N_2/MC headspace is vented through back pressure relief valves (approximately 7 inches H_2O) in ratio to the volume of liquid being filled. No estimate was provided for loading emissions.

3.1.5 Insulating Materials Manufacture

General Electric in Schenectady, New York, uses MC in the manufacture of insulating materials. General Electric considers all information concerning their process description and equipment and controls confidential.

3.1.5.1 Current Emissions and Controls[7]. Methylene chloride emissions at this facility are from a process vent and a secondary source. Total MC emissions were about 0.2 Mg in 1983. The process vent emits 0.01 Mg, while the secondary source emits 0.2 Mg. Equipment leak emissions are negligible (less than 1 kg/year). General Electric reported no discharges from pressure relief devices, no equipment opening losses, and no MC storage tanks. Methylene chloride is purchased and stored in drums. Emission sources, current controls, control efficiencies, and emission amounts are presented in Table 3-2.

3.1.6 BAYGON^R 1.5 Manufacturing

Mobay Chemicals in Kansas City, Missouri, uses MC in their Agricultural Chemicals Division as a diluent in the formulation of BAYGON^R 1.5, a pesticide. Mobay considers the process description and product packaging information confidential.

3.1.6.1 Current Emissions and Controls[4]. Total MC emissions at this facility are about 0.4 Mg/year. Emission sources, current controls, control efficiencies, and emission quantities are reported in Table 3-2.

One fixed roof storage tank emitted 0.4 Mg in 1983. However, Mobay indicated that MC is currently pumped directly from tank trucks to the process with no on-site storage. In the past, the MC was shipped to the plant in tank trucks and pumped into fixed roof storage tanks with no control devices in use.

Equipment leaks from process component leaks were 0.02 Mg in 1983. Mobay reported that BAYGON^R 1.5 is only formulated 4 or 5 days per year for 8 hours per day, and the formulation process is a closed system with a minimum of production steps. Therefore, no monitoring or repair program is conducted for MC leaks.

Mobay reported no process vent emissions, no pressure relief device discharges, no equipment opening losses, and no emissions from secondary sources. Although Mobay indicated no controls were used for unloading MC in 1983, no handling emission estimates were given.

Missouri air laws are distinguished by metropolitan area. There are regulations controlling VOC emissions from specific sources (such as solvent metal cleaning) in the Kansas City metropolitan area. However, MC is excluded from these regulations due to its negligible photochemical reactivity.

3.1.7 Specialty Chemicals[5]

Borden Chemical, in Norristown, PA uses MC in liquid chemical specialty product mixes. Borden indicated that the rate of MC consumption at their facility has been declining and is expected to continue to decline. No explanation was given for the consumption decrease.

3.1.7.1 Process Description. At Borden, MC is pumped from storage to three liquid chemical specialty mixing tanks. Following mixing, the liquid chemical specialty product, containing 30 percent MC, is sent to a "filler" where pint size cans are filled at the rate of 18 gpm. The cans are then sealed and sent to packing, warehousing and marketing.

3.1.7.2 Current Emissions and Controls[5]. Emissions from equipment leaks, storage, and handling were 3.2 Mg at this facility in 1983. The emission levels and controls are presented in Table 3-2. Equipment leaks were the largest source of emissions, contributing 2.1 Mg. Pump seals contributed 51 percent of those emissions while valves contributed 47 percent. Borden reported the entire system is readily subject to visual inspection for liquid leaks which are obvious and that these leaks are repaired "promptly". However, since Borden did not report a definitive leak repair program, equipment leak emissions were calculated assuming uncontrolled sources. Therefore, equipment leaks at this plant may be overstated. Storage facilities emitted 0.8 Mg MC. These emissions were from four fixed roof tanks including the three specialty chemical mixing tanks. Handling losses were 0.3 Mg in 1983. These losses result from the uncontrolled loading of raw MC from tank trucks to storage tanks and from evaporation of the 30 percent MC specialty chemical solution as it passes through the "filler" which puts the product into sealed cans. There are no controls for the filler process.

Pennsylvania has adopted regulations controlling emissions from storage tanks containing volatile organic compounds. MC is not specifically excluded from these regulations. Storage tanks with capacity less than or equal to 40,000 gallons which contain VOC with vapor pressure greater than 1.5 psia under actual storage conditions must be equipped with pressure relief valves. Storage tanks with capacity greater than 40,000 gallons which contain VOC with vapor pressure greater than 1.5 psia must be equipped with an external or internal floating roof or a vapor recovery system capable of recovering at least 80 percent of the vapors emitted by the tank.

Borden storage tanks range in capacity from 3,000 to 10,000 gallons. Borden did not report any conservation vents on these tanks.

3.1.8 Unidentified Production Processes

Dow Chemical, in Midland, MI operates 8 process units using MC in production. These processes are identified as processes #5 through #12. Dow indicated that all information concerning process flowcharts and end products is confidential business information. Therefore, this discussion is limited to emissions and controls used at the Dow facility.

3.1.8.1 Current Emissions and Controls[8]. Process vents and equipment leaks were the major emission sources at the Dow facility. Emissions were also reported from secondary sources, storage facilities, equipment openings, and loading and handling. In addition, Dow reported one discharge from a pressure relief device. Emissions, current controls, and control efficiencies for this facility are presented in Table 3-2.

Combined emissions from the eight process units were 1450 Mg in 1983. Emissions from process vents were 1120 Mg (77 percent of total emissions). Three process vents in process #12 emitted 811 Mg of total process vent emissions. Dow considers information on process vents and controls confidential for all processes except for an uncontrolled overheads receiver emitting 0.2 Mg/yr in process #5 and an uncontrolled storage tank emitting 129 Mg/yr in process #9. Dow reported the storage tank as a process vent. It is filled almost continuously and pumped out in batches. There are sixteen process vent emission points in the eight processes. Michigan has no regulations controlling VOC emissions from process vents.

Equipment leaks from process component leaks were 207 Mg at the Midland facility. Process components for processes #8, #10, and #12 emitted 60.1 Mg (29 percent), 27.6 Mg (13 percent), and 68.7 Mg (33 percent) respectively. Overall, the greatest sources of equipment leaks were valves (90.6 Mg, 44 percent), flanges (75.6 Mg, 37 percent), and pressure relief devices (27.2 Mg, 13 percent).

Equipment leaks are not controlled by Michigan state regulations. Monitoring programs vary widely in the degree of sophistication for different process units at this facility. Processes #11 and #12 are equipped with a continuous air monitor with 20 area sampling probes located throughout the process areas. The monitors are regularly standardized and calibrated and provide continuous sampling with time weighted average composition data. In addition to continuous air monitoring, shift personnel are responsible for 24 hour per day coverage and equipment inspection. There are also scheduled preventive maintenance inspections for all pressure relief devices and critical instruments. Shift inspection and preventive maintenance inspections are also practiced at processes #5, #7, and #9, and are the only fugitive monitoring practices at these process areas.

Process area #8 is equipped with a chromatographic air monitoring device in addition to shift inspection and annual preventive maintenance. The system is alarmed and operators have been instructed on how to respond to this alarm by finding and correcting problems.

A MC air monitoring program is conducted quarterly in the process #10 area. Dow reported a $40,000 cost plus $10,000 for maintenance. This process area is also subjected to shift inspections and an annual preventive maintenance program.

Dow indicated process #6 is experimental in nature. Therefore, equipment leak monitoring is limited to inspection by operating technicians.

Although Dow reported several monitoring and inspection programs for equipment leaks, they did not report a repair program. Therefore, equipment leak emissions were calculated using uncontrolled emission factors, and emission levels may be overstated somewhat.

Emissions from secondary sources were 88.5 Mg at the Dow facility. Dow uses biological treatment or incineration to treat or dispose of process waste streams. Emissions from incineration are negligible, therefore all secondary emissions are a result of biological treatment. Michigan does not regulate VOC emissions from secondary sources.

Storage facility emissions were 29.0 Mg in 1983. Storage tanks range in volume from 30 gallons to 47,000 gallons and include pressure vessels and fixed roof tanks. Control techniques employed include vapor return, scrubbers, carbon adsorption systems, pressure relief devices, and conservation vents. The only reported control efficiency was for vapor return, estimated by Dow as 100 percent. However, only 98 percent control efficiency is accepted without supporting test data. Michigan has adopted regulations controlling storage of organic compounds having a true vapor pressure of more than 1.5 psia, but less than 11 psia, in existing stationary vessels of more than 40,000 gallon capacity. The vapor pressure of MC at 20°C (68°F) is approximately 6.75 psia, and MC is not specifically excluded from regulation in Michigan. The regulations require that the storage tank be a pressure tank, or be equipped with a floating cover with closure seal or seals, or be equipped with a vapor recovery system capable of 90 percent recovery. Dow has one fixed roof storage tank with capacity exceeding 40,000 gallons (a 47,000 gallon tank). The tank is only equipped with a pressure relief device.

Losses from equipment openings were 4.3 Mg in 1983. Losses were reported for all processes except for process #9 where Dow indicated all equipment is drained or pumped out before maintenance work. According to Dow, the equipment is empty when opened and estimated losses are minimal. Process #12 was the largest source of equipment opening losses where 2.5 Mg MC were emitted. There are no regulations in Michigan requiring control of these emissions.

Loading and handling emissions were 2.7 Mg in 1983. Methylene chloride is received by tank truck, rail car, in drums, or through direct pipeline transfer from other processes within the Dow facility. Additionally, product containing MC from process #9 is loaded into tank cars and tank trucks. At process #5, a vapor balance line is used between tank trucks and storage tanks to prevent filling losses during transfer. At process #9, connection lines are blown empty with inert gas before disconnecting to prevent spills. Process #10 receives MC by rail car; the car is pressurized with nitrogen to help the transfer. Following transfer the rail car is vented to the atmosphere. MC is unloaded via pump at process #12. Dow reported that since pressure transfer is not used there are no loading losses. Other processes either receive MC in drums or from other processes or have "negligible" handling losses. Michigan requires submerged fill pipes in ozone attainment areas for VOC loading facilities handling 5,000,000 gal/year or more of VOC with a true vapor pressure greater than or equal to 1.5 psia.

A corrosion failure of a storage tank neck resulted in a discharge of 0.1 Mg MC to the air in 1983. Dow reported the spilled material was contained in a dike. Dow reported this corrosion failure as a pressure relief device discharge.

3.1.9 Vinyl Chloride Monomer

Methylene chloride is produced as a by-product of Vinyl Chloride Monomer (VCM) manufacturing by Shell Oil Company in Deer Park, TX. This MC is sold as light ends.

3.1.9.1 Process Description[9]. Vinyl chloride (VC) is produced by the thermal dehydrochlorination (cracking) of ethylene dichloride (EDC). The cracking of EDC occurs according to the non-catalytic reaction:

$$\underset{\text{(ethylene dichloride)}}{CH_2ClCH_2Cl} \longrightarrow \underset{\text{(vinyl chloride)}}{C_2CHCl} + \underset{\text{(hydrogen chloride)}}{HCl}$$

Operating the process at high pressures results in higher yield, fewer by-products, and allows easier separation of the VCM product from unreacted EDC and by-products.

3.1.9.2 Current Emissions and Controls[10]. Total MC emissions were 0.06 Mg at this facility. Emissions are low because Shell did not report a MC concentration greater than 0.6 percent in its process streams and 0.004 percent in its storage tanks. Therefore, process emissions, equipment leaks, and equipment opening losses were reported as minimal prior to control. In addition, Shell operates two organic chloride incinerators at the Deer Park facility. Therefore, process emissions following incineration are insignificant. Four fixed roof storage tanks are controlled by compression and incineration and have negligible emissions. The total MC emissions of 0.06 Mg resulted from an unidentified waste stream being sent to a biotreatment process. These secondary source emissions are reported in Table 3-2.

3.1.10 Plastics Production

General Electric in Pittsfield, MA, uses MC in a plastics production operation. General Electric considers information concerning process description and end products confidential.

3.1.10.1 Current Emissions and Controls[11]. Process vents and process component leaks were the major emission sources at the General Electric facility. Emissions were also reported for secondary sources, storage facilities, equipment openings, and loading and handling. Emission sources, current controls, control efficiencies, and emission levels are presented in Table 3-2.

Total methylene chloride emissions at this facility were 74.0 Mg in 1983. Emissions from process vents were 64.9 Mg MC (88 percent of total MC emissions). General Electric reported thirteen process vents with three vents controlled by condensers. A precipitation condenser vent and a dryer vacuum pump are both controlled by condensers operating at 50 percent MC removal efficiency. Emissions from these vents after control were 27.2 Mg and 9.8 Mg respectively. The precipitation condenser vent is the largest single MC emission point at the facility. A methylene chloride still vent is controlled by a condenser operating at 97 percent MC removal efficiency. Emissions from this vent were 8.2 Mg. The ten remaining process vents are uncontrolled. Emissions range from 4.6 Mg for reactor area ventilation to 0.9 Mg for the methylene chloride still water tank.

Equipment leaks resulted in MC emissions of 6.1 Mg. Valves emitted approximately 3.1 Mg MC (51 percent). Pump seals and flanges emitted 1.0 Mg (16 percent) and 0.8 Mg (13 percent), respectively. General Electric reported that there is no automated leak detection system for MC. Any significant MC leaks are generally determined by operator observation. Also, a weekly mass balance inventory is maintained for MC usage. Substantial increases over the normal process usage requirements initiates a full system investigation to determine if any leakages are occurring. Since General Electric did not report a leak repair program, uncontrolled emission factors were used to calculate equipment leak emissions, possibly resulting in an overestimate of these emissions.

Equipment opening losses were approximately 2.3 Mg in 1983. General Electric estimated this loss for approximately 2000 openings, 1300 of which were an end cap reactor nozzle opened each batch to add reactants. In addition, another reactor nozzle is opened 650 times per year. Other equipment openings involved work-up tanks, Westfalia centrifuges, filter feed tanks, filters, methylene chloride stills and separator/decant tank. General Electric provided on overall equipment opening loss estimate and did not identify emissions by specific sources.

General Electric maintains five fixed roof storage tanks containing MC. The emissions from these tanks totalled 0.3 Mg. The tanks range in volume from 250 gallons to 4100 gallons. Three of the tanks are vented to a vent condenser with 50 percent control efficiency. Two other tanks emissions are piped to a controlled tank, while one tank is uncontrolled.

Through September, 1983, MC was delivered in 55 gallon drums. The MC was pumped from the drums into dry MC tanks for process use. General Electric estimated that emissions from this operation were 0.2 Mg. In September 1983, a bulk handling system became operational. Tank truck deliveries are now made to a fixed roof 4100 gallon storage tank. The tank car feed line is connected to a pump at the storage tank base and delivered into the storage tank. Vapors are piped to the plant vent system, which condenses most of the MC vapors. General Electric reported air intake is through a cannister and a vacuum relief valve.

Two waste streams emitted about 0.2 Mg MC in 1983. The major secondary emission source is a liquid stream to a sewage treatment plant which emits 0.15 Mg of MC. A second waste stream was unidentified. This stream is contained in drums which are sent to a licensed hazardous waste disposal company. Emissions (0.01 Mg) occur when the waste stream is transferred to drums.

Massachusetts has adopted regulations for control of VOC emissions from specific sources such as surface coating operations. Methylene chloride is not specifically excluded from these regulations. However, none of the regulations are applicable to chemical production facilities.

3.2 COST OF ADDITIONAL CONTROL

Cost estimates were developed for control of process, equipment leak and storage emissions at each chemical production facility where these emissions are presently not well controlled. The cost of controlling loading and handling emissions at these facilities was not calculated since these emissions were low (4.4 Mg from all 12 facilities) and control would not be cost effective. The methodology used for estimating costs is presented in Appendix D. A summary of the cost effectiveness to control these emission sources in presented in Table 3-3 and discussed in the following sections.

Table 3-4 summarizes the estimated MC emission reductions as a function of cost effectiveness. The emission reductions are shown by the emission types as well as the total for the entire miscellaneous production category. A total emission reduction of 4200 Mg (40 percent) is technically feasible.

3.2.1 Control of Process Vent Emissions

The cost of controlling MC process vent emissions by incineration was estimated for the miscellaneous production facilities reporting process vent emissions. MC emissions can be reduced by 3780 Mg (94 percent) by incineration. The cost effectiveness of controlling MC process vent emissions ranges from a net credit of $64,800/Mg VOC at the General Electric/Mount Vernon facility to a cost of $33,000,000/Mg VOC at the General Electric/Schenectady facility where process vent emissions are only 0.012 Mg of VOC.

3.2.2 Control of Equipment Leaks

Emissions from equipment leaks totalled 550 Mg MC at the chemical plants using MC in production. As discussed in previous sections, several chemical plants have inspection programs for detection of equipment leaks, but do not mention or define repair programs. For this reason, it was assumed that no equipment leak controls were in place. Therefore, costs were estimated for adding controls at all miscellaneous production facilities except for Mobay/Kansas City, where emissions from equipment leaks were only 0.02 Mg MC. The control techniques costed are those required under the benzene fugitives NESHAP and are shown in Appendix C.

The estimated costs effectiveness for controlling equipment leak emissions range from $142/Mg of VOC to $4,320/Mg of VOC. Methylene chloride equipment leak emissions could be reduced by 49 percent (268 Mg/yr) if additional controls were used at all of the chemical production facilities.

TABLE 3-3 COST OF ADDITIONAL CONTROLS AT CHEMICAL PLANTS USING MC IN PRODUCTION

Company/Location	Emission Type	Control*	Control Efficiency (%)	MC/VOC Emission Reduction (Mg/yr)	Capital Cost $(10^3 \$)$	Recovery Credit $(10^3 \$)$	Net Annual Cost $(10^3 \$)$	Cost Effectiveness	
								MC ($/Mg)	VOC ($/Mg)
General Electric Pittsfield, MA	Process	Incineration	98	63.3/ 63.3	4,430	1,270	2,190	34,600	34,600
	Equipment leaks		59	3.6/ 6.6	17.6	2.7	9.9	2,750	1,490
	Storage	FR-PO	94	0.1/ 0.1	11.5	0.0	3.0	37,100	37,100
	Storage	COND	85	0.1/ 0.1	222	0.1	58.2	573,000	573,000
	Storage	COND	70	0.1/ 0.1	111	0.1	29.0	348,000	348,000
General Electric Mount Vernon, IN Bldg. 4	Process	Incineration	98	282/282	74,300	71,220	-18,300	-64,800	- 64,800
General Electric Mount Vernon, IN Bldg. 13	Process	Incineration	98	582/582	73,300	81,700	-24,500	-42,100	- 42,100
General Electric Mount Vernon, IN Bldg. 14/16	Process	Incineration	98	1150/1150	2,220	1170	40,500	35.2	35.2
	Equipment leaks		41	72.3/124	122	52.1	17.6	244	142
General Electric Mount Vernon, IN Bldg. 15/31	Process	Incineration	98	600/600	5,760	5,910	3,220	5,370	5,370
	Equipment leaks		74	53.4/ 80.8	156.5	34.9	26.1	490	323
	Storage	FR-SS	97	2.0/ 2.0	16.7	1.6	2.8	1,360	1,360
General Electric Schenectady, NY	Process	Incineration	98	0.01/ 0.01	1,180	0.0	402	33,000,000	33,000,000
Celanese Rock Hill, SC	Equipment leaks		49	10.8/ 17.0	30.1	7.3	15.4	1,430	904
Borden Chemical Norristown, PA	Equipment leaks		59	1.2/ 2.0	12.7	0.9	8.7	6,960	4,320
	Storage	FR-PO	94	0.4/ 0.4	11.5	0.2	2.8	7,130	7,130
	Storage	FR-PO	94	0.2/ 0.7	11.5	0.1	2.9	13,600	4,100
	Storage	FR-PO	94	0.1/ 0.3	11.5	0.0	3.0	30,300	9,100
	Storage	FR-PO	94	0.1/ 0.2	11.5	0.0	3.0	53,300	16,000
Borden Chemical Fremont, CA	Process	Incineration	98	2.2/ 2.2	5,210	708	1,160	533,000	533,000

(Continued)

TABLE 3-3 CONTINUED. COST OF ADDITIONAL CONTROLS AT CHEMICAL PLANTS USING MC IN PRODUCTION

Company/Location	Emission Type	Control*	Control Efficiency (%)	MC/VOC Emission Reduction (Mg/yr)	Capital Cost (10^3 $)	Recovery Credit (10^3 $)	Net Annual Cost (10^3 $)	Cost Effectiveness	
								MC ($/Mg)	VOC ($/Mg)
B.F. Goodrich Cleveland, OH Plant I	Equipment leaks		68	3.1/ 7.8	26.6	3.0	10.1	3,270	1,310
	Storage	FR-PO	94	0.1/ 0.1	11.6	0.1	3.0	21,100	21,100
B.F. Goodrich Cleveland, OH Plant II	Process	Incineration	98	7.3/ 7.3	1,210	0.0	3,420	56,800	56,800
	Equipment leaks		68	6.8/ 8.0	18.7	3.7	10.0	1,470	1,250
	Storage	COND	85	0.1/ 0.1	111	0.0	29.1	542,000	542,000
	Storage	COND	85	0.1/ 0.1	111	0.1	29.0	257,000	257,000
	Storage	COND	85	0.3/ 0.3	111	0.2	28.9	95,000	95,000
Dow Chemical(#5) Midland, MI	Process	Incineration	98	1.7/ 2.1	1,220	0.0	412	244,000	196,000
	Equipment leaks		58	4.8/ 7.1	16.9	3.1	8.9	1,860	1,250
Dow Chemical(#6) Midland, MI	Process	Incineration	98	65.3/ 65.3	1,210	0.0	421	6,430	6,430
	Equipment leaks		66	10.9/ 18.4	19.6	7.8	7.2	660	393
Dow Chemical(#7) Midland, MI	Process	Incineration	98	53.0/ 53.2	1,180	0.0	402	7,580	7,550
	Equipment leaks		75	4.1/ 4.7	19.2	2.2	7.9	1,910	1,670
Dow Chemical(#8) Midland, MI	Process	Incineration	98	51.5/ 53.1	2,480	1,490	1,700	33,000	32,100
	Equipment leaks		37	22.4/ 41.6	67.7	17.2	19.7	879	474
Dow Chemical(#9) Midland, MI	Process	Incineration	98	132/132	1,210	0.0	412	3,140	3,140
	Equipment leaks		56	7.4/ 8.9	16.3	4.1	8.6	1,160	965
	Storage	COND	85	0.4/ 0.4	111	0.4	28.8	65,000	65,000
	Storage	COND	85	0.1/ 0.1	111	0.1	29.0	289,000	289,000
	Storage	COND	85	0.9/ 1.5	111	0.9	28.2	31,600	19,000
	Storage[a]	FR-SS	97	125/125	39.4	102	-91.7	-733	-733
Dow Chemical(#10) Midland, MI	Process	Incineration	98	0.7/ 0.7	1,210	0.0	415	623,000	623,000
	Equipment leaks		56	15.5/ 21.3	41.2	9.4	19.1	1,240	899
	Storage	COND	85	0.8/ 0.8	111	0.7	28.4	34,300	34,300
Dow Chemical(#11) Midland, MI	Equipment leaks		44	3.0/ 8.7	18.8	3.3	11.1	3,720	1,270
	Storage	FR-PO	94	0.8/ 1.0	21.2	0.4	5.2	6,820	5,120
	Storage	FR-PO	94	0.1/ 0.3	10.6	0.0	2.7	36,900	9,200
	Storage	FR-PO	94	0.1/ 0.3	11.5	0.0	3.0	38,000	9,490

(Continued)

TABLE 3-3 CONCLUDED. COST OF ADDITIONAL CONTROLS AT CHEMICAL PLANTS USING MC IN PRODUCTION

Company/Location	Emission Type	Control*	Control Efficiency (%)	MC/VOC Emission Reduction (Mg/yr)	Capital Cost (10^3 $)	Recovery Credit (10^3 $)	Net Annual Cost (10^3 $)	Cost Effectiveness MC ($/Mg)	Cost Effectiveness VOC ($/Mg)
Dow Chemical(#12) Midland, MI	Process	Incineration	98	795/885	1,190	0.0	424.8	532	480
	Equipment leaks		31	21.1/ 44.0	22.1	17.8	16.3	770	370
	Storage	FR-SS	97	11.7/ 11.7	27.0	9.5	-2.4	-209	-209
	Storage	FR-SS	97	3.6/ 4.0	15.3	3.1	0.9	255	229
	Storage	COND	85	4.0/ 4.5	111	3.4	25.7	6,390	5,750
	Storage	FR-SS	97	1.8/ 1.8	15.3	1.4	2.6	1,460	1,460
	Storage	FR-SS	97	1.9/ 2.5	12.6	1.7	1.6	837	628
	Storage	FR-SS	97	1.0/ 2.0	16.1	1.1	3.1	3,120	1,560
Mobay Chemicals Kansas City, MO	Storage	FR-PO	94	0.4/ 0.4	14.4	0.2	3.6	9,660	9,660
Mobay Chemicals Baytown, TX	Process	Incineration	98	0.12/ 0.12	1,190	0.0	403	3,420,000	3,420,000
	Equipment leaks		54	27.4 /74.4	72.3	36.5	43.0	1,570	578

* Abbreviations

FR-SS: Floating roof with primary and secondary seals.
FR-PO: Floating roof with primary seals only.
COND: Refrigerated condenser.

[a] Storage tank discussed previously under process vent emissions.

TABLE 3-4. ESTIMATED MC EMISSION REDUCTIONS FOR OTHER CHEMICAL PLANTS AS A FUNCTION OF COST EFFECTIVENESS

	Nationwide MC Emission Reduction (Mg/Yr)			
Cost Effectiveness Range ($/Mg VOC)	Process	Equipment Leak	Storage	Total
Credit	864	-	137	1000
0 - 500	1940	208	3.6	2150
501 - 1000	---	33.7	1.9	35.6
1001 - 2000	---	25.4	4.8	30.2
2001 - 5000	132	1.2	0.2	133.4
>5000	845	---	4.7	850
TOTAL	3780	268	152	4200

3.2.3 Control of Storage Emissions

Cost estimates were developed for control of storage tanks containing MC. In 1983, emissions from these storage tanks were estimated to be 31.0 Mg/yr of MC. Three control options were evaluated: contact internal roof with a primary seal (FR-PO), contact internal roof with a secondary seal (FR-SS), and a refrigerated condenser. The most cost effective option is presented in Table 3-3.

The estimated cost effectiveness of controlling storage emissions at CFC facilities ranges from a net credit of $209/Mg of VOC to $573,000/Mg of VOC. The additional storage controls costing less than $2,000/Mg of VOC would reduce MC emissions by 27.6 Mg (85 percent).

3.3 REFERENCES

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4.0 SOLVENT DEGREASING OPERATIONS

About 10 percent (21,300 Mg) of the total methylene chloride (MC) produced in 1983 was consumed in degreasing operations. It is estimated that of this amount about 17,700 Mg were emitted to the atmosphere. Methylene chloride was used as a solvent for degreasing in a variety of industries, primarily within five distinct Standard Industrial Classifications (SIC). Emissions from degreasing operations were estimated in this study by obtaining the 1983 consumption of MC for each user industry and applying it to an emission factor derived for degreasing operations. The following sections present a brief discussion of the types of degreasers, emissions, emissions control, estimates of emissions from degreasing operations in 1983, and estimates of the costs associated with emissions control. Due to the large number of degreasing facilities in these industries, no attempt was made in this study to identify locations of individual degreasers.

4.1 INDUSTRY DESCRIPTION

Degreasing is an integral part of many industrial processes such as the manufacture of automobiles, electronics, furniture, appliances, jewelry, and plumbing fixtures. It is also used to a minor extent in the textiles, paper, plastics, and glass manufacturing industries. The degreasing process makes use of nonaqueous or aqueous solvents to clean and remove debris from a surface prior to painting, plating, assembly, repair, inspection, or other treatment. Various solvents, including petroleum distillates, chlorinated hydrocarbons, ketones, and alcohols are used either alone or in blends for degreasing purposes.[1] Five major industry groups used MC in degreasing operations. These are furniture and fixtures (SIC 25), fabricated metal products (SIC 34), electric and electronic equipment (SIC 36), transportation equipment (SIC 37), and miscellaneous manufacturing industries (SIC 39).[2]

4.2 DEGREASING EQUIPMENT

There are three basic types of degreasing equipment: cold cleaners, open top vapor degreasers, and conveyorized degreasers. Cold cleaners are usually the simplest and least expensive type of degreaser. Individual cold cleaners consist of a tank of solvent with a cover for nonuse periods. More sophisticated cold cleaners may have solvent sumps, spray nozzles, drains, and automatic controls. In the typical cold cleaning process, soiled objects are dipped into the solvent bath until the soils are dissolved from the surface. The cleaning process can be enhanced by agitating the solvent, and brushing or spraying soiled parts. Solvents are normally used at room temperature, but in some applications may be heated to a temperature below the boiling point of the solvent.[1]

Open top vapor degreasers are similar in configuration to cold cleaners but are operated in a different manner. Open top vapor degreasers are operated at an elevated temperature to boil the solvent. The vapors from the boiling solvent condense on and clean soiled objects. A typical open top vapor degreaser consists of a tank equipped with a heating and cooling system. The heating coils on the inside bottom of the tank boil the solvent, thereby generating the vapors needed for cleaning. Cooling coils located near the top and on the inside perimeter of the tank condense solvent vapors, preventing them from diffusing out of the tank. Thus, a controlled vapor zone is created within the tank. Soiled objects are lowered into the vapor zone where solvent condenses on their surfaces and dissolves the soils. When condensation ceases, the cleaned objects are withdrawn. Only halogenated solvents are used for vapor degreasing because, in addition to their excellent cleaning properties, they are nonflammable and because their heavy vapors can be easily contained within the machine.[1]

Conveyorized degreasers feature automated conveying systems for continuous cleaning of parts. Conveyorized degreasers clean either by cold cleaning or vapor degreasing, although most clean using vaporized solvent. While these units tend to be the largest degreasers, they are enclosed systems and actually produce less emissions per part cleaned than other types of degreasers.[1]

4.3 EMISSIONS FROM DEGREASING OPERATIONS

National emission estimates for degreasing operations were calculated from 1983 MC consumption data provided by the Halogenated Solvents Industry Alliance (HSIA).[2] The consumption data were used in conjunction with emission factors generated from available literature to estimate nationwide emissions.[1] A brief description of the estimation procedure follows.

Available data indicate that 67 percent of all MC consumed in degreasing operations is used in cold cleaning while about 33 percent is used in vapor degreasing.[3] Previous EPA studies estimated that for every kg of a solvent used in cold cleaning, 0.43 kg are emitted. The corresponding emission factor for open top vapor degreasing is 0.785 kg/kg consumed and for conveyorized degreasing is 0.85 kg/kg consumed.[4] Assuming that vapor degreasing use of MC is divided equally between open top and conveyorized degreasing processes, a weighted average emission factor of 0.56 kg/kg MC consumed was calculated. It was assumed that the remaining 0.44 kg/kg MC consumed would be recycled.

Based on information from solvent recyclers,[5] it was estimated that about 75 percent of all waste solvent from degreasing (0.44 kg/kg MC consumed) is recovered and reused. Therefore, total MC consumption by a degreaser equals consumption of fresh solvent plus consumption of recycled solvent. As before, 0.56 kg/kg of the recycled solvent is emitted. Taking into account the emission of recycled solvent, it is estimated that for every kg of fresh MC used in degreasing, 0.83 kg is emitted. The remaining 0.17 kg is assumed to be either incinerated or disposed of in a landfill according to applicable regulations. Appendix C presents the details of these material balance calculations.

The total 1983 MC emissions for each of the five SICs were estimated by applying the 0.83 kg factor to the 1983 MC consumption figure. Table 4-1 shows the estimated MC emissions from degreasing operations in these industries.

TABLE 4-1. 1983 MC EMISSIONS FROM DEGREASING OPERATIONS, BY INDUSTRY

Industry (SIC Code)	Emissions (Mg/yr)
Furniture and Fixtures (25)	1,140
Fabricated Products (34)	4,130
Electrical and Electronic Equipment (36)	4,910
Transportation Equipment (37)	2,170
Miscellaneous Manufacturing Industries (39)	5,360
TOTAL	17,700

Emissions were also estimated for each State in the U.S. The MC emissions were estimated by assuming that emissions are proportional to the number of employees for a given industry in each State. The total number of employees in each of the five industry groups was estimated from U.S. Department of Commerce data.[6] For example, the emissions in Illinois from the fabricated products manufacturing industry (SIC 25) were estimated as follows:

- Furniture and fixtures manufacturing consumption of MC in 1983 = 1,370 Mg.
- $1{,}370 \text{ Mg} \times 0.83 \dfrac{\text{Mg emitted}}{\text{Mg consumed}} = 1{,}140 \text{ Mg emitted.}$
- The number of employees within the furniture and fixtures manufacturing industry for Illinois = 18,700.
- Total number of employees within the furniture and fixtures manufacturing industry = 438,000.
- $\text{Illinois emissions} = 1{,}140 \times \dfrac{18{,}700}{438{,}000} = 50 \text{ Mg}$

This procedure was followed for each industry identified to use MC in degreasing operations. The totals for industry groups were then aggregated for each state. The results are presented in Table 4-2.

4.4 EMISSIONS CONTROL

Control methods specified in the CTG and BID for degreasing are summarized in Table 4-3.[1,7] These methods include add-on equipment as well as improved work practices.

Add-on equipment for control of degreaser emissions includes adding covers to equipment openings, increasing freeboard area, adding freeboard chillers, and providing drainage racks for parts. These

TABLE 4-2. 1983 METHYLENE CHLORIDE EMISSIONS FROM DEGREASING OPERATIONS, BY STATE

State	Emissions (Mg)	State	Emissions (Mg)
Alabama	240	Montana	5
Alaska	1	Nebraska	70
Arizona	180	Nevada	30
Arkansas	140	New Hampshire	100
California	2,320	New Jersey	760
Colorado	190	New Mexico	30
Connecticut	500	New York	1,470
Delaware	20	North Carolina	550
District of Columbia	3	North Dakota	10
Florida	490	Ohio	930
Georgia	280	Oklahoma	160
Hawaii	10	Oregon	70
Idaho	10	Pennsylvania	940
Illinois	1,180	Puerto Rico	140
Indiana	610	Rhode Island	400
Iowa	230	South Carolina	160
Kansas	130	South Dakota	20
Kentucky	200	Tennessee	410
Louisiana	140	Texas	880
Maine	60	Utah	60
Maryland	200	Vermont	50
Massachusetts	700	Virginia	260
Michigan	810	Washington	250
Minnesota	280	West Virginia	40
Mississippi	200	Wisconsin	440
Missouri	370	Wyoming	1
		TOTAL	17,700

TABLE 4-3. EXAMPLE CONTROL TECHNIQUES FOR DEGREASERS

Degreaser Type	Control Devices	Operating Practices
Cold Cleaners	Cover for tank Parts drainage rack Raised freeboard[a]	Keep cover closed when degreaser not in use Fully drain cleaned parts
Vapor Degreasers	Cover for tank Freeboard chiller[b] Raised freeboard Carbon adsorber	Keep cover closed when degreaser not in use Fully drain cleaned parts Move parts slowly into and out of degreaser
Conveyorized Degreasers	Port Covers Freeboard chillers Carbon adsorbers	Maintain conveyor at moderate speed Keep exhaust ventilation rates moderate

[a] Freeboard is the distance from the liquid solvent surface or top of the solvent vapor to the lip of the tank. "Raised freeboard" is a physical extension of the freeboard to reduce drafts, and thereby solvent evaporation, within the degreaser.

[b] Additional cooling coils above the primary coils to further inhibit the diffusion of solvent vapors to the atmosphere.

devices limit evaporation losses from solvent baths and solvent carry-out. More sophisticated control techniques include carbon adsorption to recover solvent vapors.

Work practices can be improved to limit solvent emissions from degreasing. These improvements, characterized by practices that reduce solvent exposure to the atmosphere, include: keeping degreaser covers closed, fully draining parts prior to removal from degreaser, maintaining moderate conveyor speeds, and keeping ventilation rates moderate.

4.5 COST OF EMISSIONS CONTROL

The costs for controlling emissions from model degreasing facilities have been estimated in previous EPA-sponsored studies.[7,8,9] The purpose of the cost evaluation effort for this document is to update the costs presented in the earlier EPA studies. Costs are presented for a representative size degreaser for each of three degreaser types: (1) cold cleaners, (2) open top vapor degreasers, and (3) conveyorized vapor degreasers. The cost estimates are for retrofitting existing degreasing facilities. Tables 4-4, 4-5, and 4-6 present the retrofit cost estimates for cold cleaners, open top vapor degreasers, and conveyorized vapor degreasers, respectively. The costs estimated in the previous EPA study are in fourth quarter 1980 dollars. These costs were updated to fourth quarter 1984 dollars using the plant cost indexes (323.6/269.7=1.2).[10,11]

Several assumptions concerning degreaser operating parameters were made in developing costs for controlling emissions from the three types of degreasers. It was necessary to assume operating parameters for typical uncontrolled and controlled degreasers so that average emission reductions for each type of degreaser could be determined.

In developing cold cleaner control costs the degreaser size was assumed to be 0.4 m^2 and the annual period of operation was assumed to be 500 hours (2 hrs/day, 5 days/week, 50 wks per year). The uncontrolled emissions were based on a cold cleaner with a 0.3 freeboard ratio and a manual cover. Total emissions from this uncontrolled cold

TABLE 4-4. RETROFIT CONTROL COSTS FOR COLD CLEANERS
(FOURTH QUARTER 1984 DOLLARS)

Cost Component	0.7 FBR,[a] Manual Cover and Drain
Capital Costs, ($)	
Freeboard (installed)	357
Drain	25
Installation Costs, $	
Freeboard (in purchase cost)	
Drain	13
Annual Operating Costs, #/yr	
Capital Charges[b]	47
Administration, Insurance, and Taxes[c]	14
Added Labor[d]	285
Maintenance[e]	11
Utilities	0
Total Annualized Cash, $/Yr	
Emission Reduction, Mg/Yr	0.4
Recovered Solvent Credit, $/Yr[f]	194
Net Annualized Cost, $/Yr	163
Cost Effectiveness, $/Mg	410

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[a] Freeboard ratio.

[b] Total Installed Capital Cost annualized over 15 years at a 10 percent interest rate.

[c] Four percent of total installed capital cost.

[d] Labor due to drain time requirement, based on 20 loads per day, 15 second drain time per load.

[e] Three percent of total installed capital cost.

[f] Based on solvent price of $0.485 per kilogram.

TABLE 4-5. RETROFIT CONTROLS COSTS FOR OPEN TOP VAPOR DEGREASERS (FOURTH QUARTER 1984 DOLLARS)

	Cover 0.75 FBR[a]	Automatic Cover 0.75 FBR	Cover Above Freezing FBC[b,c]	Cover Below Freezing FBC[c]	Cover, Carbon Adsorber
Capital Costs, $					
Cover	1,238	3,832	1,238	1,238	1,238
0.75 Freeboard	1,012	268	1,012	1,012	1,012
Refrig. Freeboard	-	-	-	-	-
Carbon Adsorber	-	-	-	-	-
Auxiliary Equipment	595	595	595	595	595
Added Plant Space	-	-	-	-	-
Installation Costs, $					
Cover	136	203	136	136	136
0.75 Freeboard	136	136	136	136	136
Refrig. Freeboard	-	-	-	-	-
Carbon Adsorber	-	-	-	-	5,950
Auxiliary Equipment	136	136	136	136	136
Total Capital Costs, $	3,253	5,170	8,499	13,021	18,366
Operating Costs, $/yr					
Capital Charges $/yr.[d]	427	679	1,117	1,711	2,413
Administration, Ins., Taxes[e]	130	207	45	68	97
Maintenance[f]	98	155	34	51	72
Added Labor	570	-	570	570	570
Utilities					
Electricity	-	-	71	98	208
Steam	-	-	-	-	201
Water	-	-	-	-	26

(continued)

TABLE 4-5 CONCLUDED. RETROFIT CONTROLS COSTS FOR OPEN TOP VAPOR DEGREASERS (FOURTH QUARTER 1984 DOLLARS)

	Cover 0.75 FBR[a]	Automatic Cover 0.75 FBR	Cover Above Freezing FBC[b,c]	Cover Below Freezing FBC[c]	Cover, Carbon Adsorber
Total Annualized Costs, $/Yr	1,225	1,041	1,837	2,498	3,587
Emission reduction, Mg/yr	1.84	2.86	3.19	3.19	3.89
Recovered solvent credit, $/yrs	892	1,387	1,547	1,547	1,887
Net annual control cost, $/yr	333	-346	290	951	1,700
Cost Effectiveness, $/Mg	180	10	90	300	440

[a] Freeboard Ratio.

[b] Refrigerated freeboard chiller.

[c] Also require 0.75 freeboard ratio.

[d] Total installed capital cost annualized over 15 years at a 10 percent interest rate.

[e] Four percent of total installed capital cost.

[f] Three percent of total installed capital cost.

[g] Based on solvent price of $0.485 per kilogram.

TABLE 4-6. RETROFIT CONTROL COSTS FOR CONVEYORIZED DEGREASERS
(FOURTH QUARTER 1984 DOLLARS)

	RFC[a]	Carbon Adsorber	Adsorber Drying Tunnel
Capital Costs, $			
Refrig. Freeboard	14,994	0	0
Carbon Adsorber	0	58,310	58,310
Auxiliary	0	0	11,900
Installation Costs, $			
Refrig. Freeboard	407	0	0
Carbon Adsorber	0	11,900	11,900
Auxiliary Equipment	0	0	2,380
Additional Plant Space	175	4,998	5,998
Total Capital Costs, $	15,576	75,208	90,488
Operating Costs, $/Yr			
Capital Charges[6]	2,047	9,882	11,890
Adm., Ins., & Taxes[c]	623	3,008	3,620
Operating Labor	0	0	0
Maintenance[d]	467	2,256	2,715
Utilities			
Electricity	195	277	277
Steam	-	626	626
Cooling Water	-	62	62
Total Annualized Cost, $/Yr	3,332	16,111	19,190
Emission Reduction, Mg/Yr	9.84	10.9	12.4
Recovered Solvent Credit, $/Yr[e]	4,772	5,287	6,014
Net Annualized Costs, $/Yr	-1,440	10,824	13,176
Cost of Control, $/Mg	-150	990	1,060

[a] Refrigerated freeboard chiller.

[b] Total installed capital cost annualized over 5 years at a 10 percent interest rate.

[c] Four percent of total installed capital cost.

[d] Three percent of total isntalled capital cost.

[e] Based on solvent price of $0.485 per kilogram.

cleaner were estimated to be 1,140 kg/yr. The controlled emissions were based on a cold cleaner with a 0.75 freeboard ratio, a manual cover and a drainage rack. Total emissions from this cold cleaner were estimated to be 740 kg/yr. It is estimated that a 35 percent emissions reduction can be achieved with a raised freeboard, a manual cover, and a drainage rack.[9,12,13]

For open top vapor degreaser (OTVD) control cost development degreaser size was assumed to be 1.5 m^2 and an operating schedule of 1,500 hours (6 hrs/day, 5 days/wk, 50 wks/yr) was used. The uncontrolled emissions were based on an OTVD with a freeboard ratio of 0.5 and were estimated to be 8,770 kg/yr. This estimate assumes an 8-hour working day during which the degreaser is uncovered for 6 of these hours; the degreaser is idle for the remaining 2 hours. Five control options for OTVDs were investigated, including covers and raised freeboards, automated covers and raised freeboards, above-freezing refrigerated chillers, below freezing refrigerated chillers, and carbon adsorption systems. The control costs are presented in Table 4-5, and are based on the following: (1) utilization of a cover with a control efficiency of 90 percent during idle time; (2) reduction of 15 percent in vaporization losses by increasing the freeboard ratio from 0.5 to 0.75; (3) reduction of 40 percent in vaporization losses by use of either above- or below-freezing chillers; (4) reduction of 40 percent in vaporization losses due to the use of an automated cover; (5) reduction of 65 percent in vaporization losses due to the use of a carbon adsorber; and (6) a 10 percent reduction in carry out losses due to use of a refrigerated freeboard device. Overall achievable emission reductions with these techniques were estimated to range from 21 percent to 44 percent.[9,12,13]

Conveyorized degreaser control cost estimates were based on a degreaser 3.0 m^2 in size with an operating schedule of 2,000 hours. (8 hrs/day, 5 days/wk, 50 wks/yr) Uncontrolled emissions for a typical conveyorized degreaser were estimated to be about 21,800 kg/yr. Three control options were examined for costing purposes, including refrigerated freeboard chillers, carbon adsorbers, and carbon adsorbers along with a drying tunnel. Control costs are presented in

Table 4-6 and are based on the following: (1) a 45 percent reduction in solvent loss due to the use of refrigerated freeboard chillers; (2) a 50 percent reduction in solvent loss due to the use of a carbon adsorber; and (3) a 15 percent reduction in carry-out emissions only, due to the use of a drying tunnel. Achievable emission reductions using these techniques are estimated to range from 45 percent to 57 percent.[9,12,13]

Estimates of the national emission reduction associated with controlling MC emissions from degreasers were made using: (1) emission factors developed for uncontrolled cold cleaners, open top vapor degreasers, and conveyorized vapor degreasers; and (2) the estimated total number of uncontrolled degreasers in MC service in 1983. It is estimated that about 6,590 Mg/yr MC emissions can be reduced by the application of control techniques on uncontrolled cold cleaners, open top vapor degreasers, and conveyorized vapor degreasers. This represents a 37 percent reduction in MC emissions from degreasers. Potential MC emission reductions for each type of degreaser are 2,360 Mg/yr (cold cleaners), 1,770 Mg/yr (open top vapor degreasers), and 2,460 Mg/yr (conveyorized vapor degreasers). The details of the calculations for estimating national emission reduction are presented in Appendix D.

4.6 REGULATORY REQUIREMENTS

EPA has approved RACT guidelines for solvent degreasing operations that have been adopted by 32 States and the District of Columbia. The 10 States that have the highest estimated emissions of MC from solvent degreasing, California, Ohio, New York, Michigan, Illinois, Pennsylvania, Indiana, Texas, Massachusetts, and New Jersey, have all adopted EPA-approved RACT. These 10 States account for about 59 percent of total degreasing emissions of MC. In addition, EPA has proposed (but not promulgated) an NSPS that would control emissions from new solvent degreasers.

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5.0 PHOTORESIST STRIPPING OPERATIONS

About five percent of the methylene chloride (MC) produced in 1983 was used as a photoresist stripping solvent in the electronics industry during the production of printed circuit boards. It was not within the scope of this study to make direct contact with all manufacturers of printed circuit boards or to verify the exact number of facilities presently in operation. Emissions from photoresist stripping operations in printed circuit board manufacturing were estimated in this study by obtaining the 1983 MC consumption for printed circuit board manufacturing and applying an emission factor derived for photoresist stripping operations. It is estimated that in 1983, about 11,900 Mg of MC were consumed in photoresist stripping operations and about 6,800 Mg were emitted to the atmosphere.

5.1 INDUSTRY DESCRIPTION

Photoresist stripping is an operation used in the electronics industry during the production of printed circuit boards. The processing of copper-clad laminated circuit boards into printed circuit boards occurs in several basic steps. First, a polymer-based photoresist chemical is applied to the entire circuit board surface and is masked with the appropriate design. Next, the photoresist is exposed to light. Further, the photoresist is developed using a solvent to remove unwanted resist. Finally, the exposed copper is etched with acid and the remaining resist is stripped away with methylene chloride.[1]

Three types of systems are employed in the production of printed circuit boards. These are (a) solvent systems, which use methylene chloride as the stripper solvent and 1,1,1-trichloroethane as the developer solvent; (b) semi-aqueous systems; and (c) aqueous systems. The semi-aqueous system and aqueous systems do not use methylene chloride as a stripper solvent. Solvent systems may use pure methylene chloride or a blend of methylene chloride, with an alcohol (usually methanol) as the stripper solvent.

Overall, there is a trend away from solvent stripping systems toward semi-aqueous or aqueous systems. This has been due primarily to the growing concern for minimizing exposure to halogenated hydrocarbon solvents. Further, solvent systems have higher operating costs because of high solvent costs, solvent recovery equipment costs, and waste disposal expenses.[1] However, despite the fact that there is a trend away from solvent systems, there is indication that for printed circuit boards requiring high resolution, solvent systems will continue to be used.[2]

5.2 EMISSIONS AND CONTROL TECHNIQUES

National emission estimates for photoresist stripping operations were calculated from 1983 MC consumption data provided by the Halogenated Solvents Industry Alliance (HSIA).[3] The consumption data were used in conjunction with an emission factor generated from industry contacts.

Based on information from an industry representative, it was estimated that for every kg of methylene chloride consumed in photoresist stripping 0.25 kg is emitted directly to the atmosphere.[4] It was assumed that the remaining 0.75 kg/kg of methylene chloride goes to recycling. Further, information from solvent recyclers indicates that about 75 percent of all recycled solvent from photoresist stripping is recovered and reused. Therefore, total MC consumption in photoresist stripping equals consumption of fresh solvent plus consumption of recycled solvent. As before 0.25 kg/kg of the recycled solvent is emitted. Taking into account the emission of recycled solvent, it is estimated that for every kg of fresh solvent used in photoresist stripping, 0.57 kg is emitted. Appendix C presents the details of these material balance calculations. The remaining 0.43 kg is assumed to be either incinerated or disposed of in a landfill according to applicable regulations.

The total 1983 MC emissions for photoresist stripping were estimated for each State in the U.S. The MC emissions were estimated by assuming that emissions are proportional to the number of employees for the printed circuit board manufacturing industry in each State. The total number of employees in printed circuit board manufacturing was estimated from U.S. Department of Commerce data.[5] For example the emissions in Illinois were estimated as follows:

- Printed circuit board manufacturing nationwide consumption of MC in 1983 = 11,900 Mg
- 11,900 Mg x 0.57 $\frac{\text{Mg emitted}}{\text{Mg consumed}}$ = 6,800 Mg nationwide emissions
- The number of employees within printed circuit board manufacturing in Illinois = 11,600
- Total number of employees within printed circuit board manufacturing industry = 215,000
- Illinois emissions = 6,800 Mg x $\frac{11,600}{215,000}$ = 370 Mg

This procedure was followed for each State and the results are presented in Table 5-1.

A broad survey of individual facilities using MC was not conducted regarding controls commonly applied within the industry. Consequently, the current status of control technology could not be ascertained. However, one printed circuit board manufacturer indicated that carbon adsorption was being used to control MC emissions from photoresist stripping operations.[6]

5.3 REGULATORY REQUIREMENTS

Currently only California has regulations affecting photoresist stripping operations in printed circuit board manufacturing. However, MC is exempt from these regulations because it is not considered to be an ozone precursor.

TABLE 5-1. 1983 METHYLENE CHLORIDE EMISSIONS FROM PHOTORESIST STRIPPING OPERATIONS, BY STATE

State	Emissions (Mg)	State	Emissions (Mg)
Alabama	130	Montana	0
Alaska	1	Nebraska	5
Arizona	70	Nevada	5
Arkansas	5	New Hampshire	130
California	1,910	New Jersey	340
Colorado	70	New Mexico	10
Connecticut	250	New York	1,020
Delaware	20	North Carolina	30
District of Columbia	5	North Dakota	5
Florida	260	Ohio	140
Georgia	20	Oklahoma	60
Hawaii	20	Oregon	50
Idaho	5	Pennsylvania	290
Illinois	370	Puerto Rico	120
Indiana	40	Rhode Island	40
Iowa	30	South Carolina	15
Kansas	20	South Dakota	5
Kentucky	10	Tennessee	30
Louisiana	0	Texas	160
Maine	30	Utah	0
Maryland	50	Vermont	5
Massachusetts	570	Virginia	50
Michigan	50	Washington	0
Minnesota	200	West Virginia	0
Mississippi	5	Wisconsin	40
Missouri	60	Wyoming	0
		TOTAL	6,800

5.4 REFERENCES

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6.0 FOAM MANUFACTURING

The foam manufacturing industry consumed about 7 percent (14,200 Mg) of the methylene chloride (MC) produced in 1983. It is estimated that 100 percent of the MC consumed in foam manufacturing was emitted to the atmosphere.

There have been 85 foam manufacturing plants in the United States identified by this study. The States having the most manufacturers are California (12 plants), Texas (10 plants), North Carolina (7 plants), Indiana (6 plants), and Mississippi (6 plants).[1] It is unlikely that all of these foam plants consume, and thus, emit MC. However, it was not within the scope of this study to identify the locations of all foam manufacturing plants using MC.

6.1 INDUSTRY DESCRIPTION

Methylene chloride is used as an auxiliary blowing agent in the production of flexible urethane foam slabstock. The primary blowing agent is carbon dioxide which forms from the reaction of two basic formulation ingredients of the foam. Auxiliary blowing agents are used when softer foams are required. The cushioning nature of the foam is due to minute foam cells that are formed by the gaseous blowing agents. It has been reported that most foam manufacturing facilities have traditionally used CFC-11 as the auxiliary blowing agent.[2] MC is also used often because it is a relatively inexpensive agent compared to CFC-11. However, its higher boiling point requires more heat to initiate reaction than do chlorofluorocarbons and thus the reaction is more difficult to control.[1]

Methylene chloride and other ingredients are pumped to a mixing head and discharge nozzle positioned at the opening of a foam tunnel. The material is then expelled onto a conveyor belt within the foam tunnel. The exothermic reaction of materials in the tunnel vaporizes the blowing agent, forming cells in the foam. This curing process continues as the material passes through the tunnel, exiting as formed slabstock ready to be sawed into slabs and later packaged for shipment.[1]

6.2 CURRENT EMISSIONS AND CONTROLS

Methylene Chloride emissions result from vaporization in the foam tunnel primarily, but also may result from storage tanks, equipment leaks and vaporization of residual MC in the foam curing area. Based on information from an industry representative it is estimated that well over 50 percent of MC emissions from foam manufacturing processes are from the foam tunnel itself, with the remainder emitted during storage, transfer, or use.[3] Industry contacts have indicated the foam plants are typically uncontrolled.[3,4]

The Halogenated Solvents Industry Alliance reported that the foam blowing industry consumed approximately 14,200 Mg of MC in 1983.[5] It was assumed for the purposes of this study that all MC consumed is eventually emitted to the atmosphere. Emissions from foam manufacturing are presented by State in Table 6-1. These emission estimates are estimated by State according to the consumption distribution provided by HSIA.

Table 6-1. 1983 MC EMISSIONS FROM FOAM MANUFACTURING, BY STATE

STATES	ANNUAL EMISSIONS (Mg)
Arkansas	340
California	3,060
Colorodo	120
Florida	350
Georgia	670
Hawaii	120
Illinois	370
Indiana	690
Kentucky	120
Maryland	230
Massachusetts	230
Michigan	540
Minnesota	120
Mississippi	960
Ohio	230
Oregon	300
Pennsylvania	580
New Jersey	230
New York	120
North Carolina	1,970
Rhode Island	780
South Carolina	120
Tennessee	610
Texas	1,130
Virginia	110
Washington	100
TOTAL	14,200

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7.0 PHARMACEUTICAL MANUFACTURING

The pharmaceutical industry used approximately 6 percent (13,200 Mg) of total methylene chloride (MC) production in 1983. Methylene chloride is used in pharmaceutical manufacturing as a general solvent, as an extraction solvent, and in tablet coatings. Previous EPA studies indicate that there are over 800 pharmaceutical plants in the United States and its territories[1], although only a fraction of these plants likely use MC. Prior EPA reports indicate that in addition to its use in tablet coatings, MC is used in the manufacture of antibiotics, steroids, and vitamins, and specifically in the production of reserpine, cephalothin, cephaliride, cepharin, tolbutamide, and estrone.[2,3] The exact locations of all pharmaceutical plants using MC have not been identified in this study.

7.1 INDUSTRY DESCRIPTION

Pharmaceuticals typically are manufactured in a series of batch operations. The following description represents a likely sequence of operations. The solvent is received and stored in tanks ranging from 20,000 to 110,000 liters (5,280 to 29,100 gallons) capacity. From storage the solvent is piped directly to a glass - or stainless steel-lined reactor. A typical batch reactor has a capacity of 2,000 to 11,000 liters (500-3000 gallons). To begin a production cycle, the reactor is washed and dried with the solvent. After washing occurs, air or nitrogen is commonly used to purge the reactor. Solid reactants and solvent are then charged to the reactor which is equipped with a condenser. After the reaction cycle is finished, the unreacted volatile compounds and remaining solvent are cleared from the reactor through distillation and condensation. The crude product is then transferred to a holding tank where it is washed with water or solvent to remove any remaining reactants or by-products. Next, the crude product undergoes one of several separation processes.

Typical separation processes include distillation, extraction, and filtering. The crude product may then be dissolved in another solvent and transferred to a crystallizer for purification. After crystallization, the solid material may be separated from the remaining solvent by centrifugation. While in the centrifuge, the product may be washed again with water or solvent. Tray, rotary, or fluid-bed dryers are then used for final product finishing.[1]

7.2 CURRENT EMISSIONS AND CONTROLS

At pharmaceutical plants where MC is used as a solvent, each operation within the manufacturing process, as well as the storage and handling steps, may be sources of MC emissions. The level of emissions varies significantly among different operations and depends on the quantity of solvent used, the type of equipment performing the operation, and the frequency of performing the operation. Dryers are potentially large emission sources. Emission rates from dryers vary depending on the size of the unit, the number and duration of drying cycles per year, and the amount of MC evaporated during a given drying cycle. Emissions from reactors result from the displacement of MC-laden air during reactor charging, as well as from solvent evaporation during the reaction cycle, the venting of uncondensed MC from overhead condensers during refluxing, from the purging of vaporized MC following solvent wash, and from the opening of reactors during the cycle for sampling. Distillation columns emit MC as uncondensed solvent. Storage and handling emissions result from displacement of vapors during storage tank filling and from displacement of vapors within the storage tank when temperature or atmospheric pressure changes occur.[1]

A survey of 17 ethical drug manufacturers in 1982 indicated a total annual MC purchase of about 11,400 Mg by these manufacturers. The responding firms were estimated to represent approximately one-half of the production of ethical domestic pharmaceuticals in 1982. The estimated final disposition of the above total MC usage was the following: 4,900 Mg air emissions (43 percent); 570 Mg sewer disposal (5 percent); 4,330 Mg incinerated (38 percent); 1,250 Mg contract hauled

(11 percent); and 340 Mg disposed of off-site (3 percent).[4] Assuming the same disposition for 1983 consumption provided by the Halogenated Solvents Industry Alliance, estimated air emissions are 5,700 Mg.[5]

Individual facilities using MC were not contacted regarding the control techniques commonly used within the industry. Consequently, the current status of control technology for pharmaceutical manufacturing could not be ascertained. However, the controls available to the industry include condensers, absorbers, carbon adsorbers and, in some cases, incinerators. Storage and transfer emissions can be controlled by vapor return lines, conservation vents, vent scrubbers, pressurized storage tanks, and floating roof storage tanks.[1]

7.3 REFERENCES

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8.0 PESTICIDE MANUFACTURING

Pesticide manufacturing accounted for about one percent (2,700 Mg) of total methylene chloride (MC) consumption in 1983.[1] Methylene chloride has several applications in the pesticide industry. It is used for extraction, phase separations, purifications, crystallization, and as a general transport solvent.[2,3,4] Previous studies indicate that there are about 140 individual pesticide facilities in the United States manufacturing one or more pesticides.[5] Of these, a fraction are users of MC.

According to information provided by the Halogenated Solvents Industry Alliance (HSIA), pesticide facilities in three cities accounted for about 77 percent of total 1983 use of MC in pesticide production.[1] The facilities in these cities were identified from a list of pesticide manufacturers in the available literature.[6] No attempt was made in this study to verify the amount of MC used by these facilities.

Three additional pesticide facilities accounting for about 2 percent of total MC production in 1983 were identified directly through a telephone survey.[2,3] The identified pesticide facilities and associated 1983 methylene chloride consumption volumes are presented in Table 8-1.

8.1 INDUSTRY DESCRIPTION

The methods and exact technology for manufacturing pesticides varies considerably depending on the type of pesticide. The pesticide industry employs the same unit processes and operations used in the chemical processing industry. These include chemical reactions, filtering, separation operations, condensation, and drying. Production processes are usually carried out at ambient or slightly above ambient temperatures. Elemental chlorine is the raw material common to most pesticide production and is also frequently used to prepare other raw material used for pesticide production. The raw materials, intermediates, by-products, and products may be highly toxic to certain plants and animals, including man.[5]

TABLE 8-1. 1983 CONSUMPTION OF METHYLENE CHLORIDE IN PESTICIDE MANUFACTURING

Company/Location	Consumption/Emissions (Mg/yr)
Chevron Chemical Company Richmond, CA	740
Union Carbide Woodbine, GA	1060
Great Lakes Chemical Company El Dorado, AR	265
Buckman Laboratories Memphis, TN	26
Buckman Laboratories Cadet, MO	7
Rhone-Poulenc Chemical Company Mt. Pleasant, TN	12
Unidentified	590
TOTAL	2,700

8.2 EMISSIONS AND CONTROLS

Air emissions from pesticide facilities include particulates, gases, and vapors which may emanate from process equipment at each step of the manufacturing process. There is indication that evaporation of wastewater from holding ponds may be a significant source, although few quantitative data are available.[5] The limited data gathered in this source assessment study indicate that primary MC emission sources are equipment leaks, and waste treatment facilities as well as emissions from control devices such as condensers and scrubbers.[2,3,4] It is likely that most of the MC consumption in pesticide manufacturing is emitted to the atmoshpere. In this study it was assumed that all the MC consumed in pesticide manufacturing during 1983 was emitted.

It was not within the scope of this study to undertake a comprehensive survey of the control techniques commonly used within the industry. Consequently, typical control levels for pesticide manufacturing could not be ascertained. However, the control techniques employed by two pesticide facilities using MC that were contacted include condensers, recycling systems, refrigerated condensers, and incinerators.[2,4]

8.3 REFERENCES

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6. SRI Directory of Chemical Producers-1983. SRI International. Menlo Park, California.

9.0 DISTRIBUTION FACILITIES

Virtually all methylene chloride (MC) produced is sold through chemical distributors. There are an estimated 300 chemical distributors handling chlorinated solvents. Table 9-1 presents the five largest MC distributors. These distributors handle about 40 percent of the total MC sold through distributors. In general, distributors maintain as few as three to as many as 65 regional distribution facilities spread out across the nation. One chemical distributor estimated the number of regional distribution facilities at 500 nationwide.[2] Each district distributor receives chemicals directly from the producer by tank truck or railcar. Transportation is provided by the distributor. The received chemicals are stored by district distributors in 8,000 to 20,000 gallon fixed-roof storage tanks. The storage tanks used by district distributors include vertical, horizontal, and underground tanks. Turnover times for storage tanks typically range from 2 weeks to a little over a month. Although the exact number of distributors and distribution facilities that handle MC is not known, it is estimated that there are 109 MC storage tanks owned by distributors, the majority of which are fixed roof tanks. The procedure used to estimate the number of tanks is given in Appendix E.

9.1 EMISSIONS FROM DISTRIBUTION FACILITIES

Emissions from distribution facilities can be categorized as two types, storage and handling. Storage emissions include breathing and working losses from tanks. Handling emissions result from vapor displacement when drums and tank trucks are filled.

Storage and handling emissions of MC from distribution facilities were estimated using AP-42 emission factors[4] and data supplied by the major distributors. The details of those calculations are presented in Appendix E. It is estimated that approximately 490 Mg of MC were emitted in 1983 from distribution facilities. Storage emissions accounted for 280 Mg, while handling emissions were about 210 Mg.

9.2 REGULATORY REQUIREMENTS

There are State and Federal regulations that may affect methylene chloride distribution facilities. Most States have regulations for storage and handling of volatile organic liquids (VOL). However, many of these States exclude MC from their VOL regulations due to its low photochemical reactivity. Also, a Federal regulation for volatile organic liquid storage has been proposed. However, these regulations generally apply to storage tanks with a volume of 25,000 gallons or greater. According to the major distributors of MC, the size of MC storage tanks is typically 15,000 gallons or less.[5]

TABLE 9-1. SUMMARY OF MAJOR METHYLENE CHLORIDE DISTRIBUTORS

Company	Number Of Distribution Facilities	Number Of MC Storage Tanks	Typical Size (Gal)	Typical Size Turnover
Ashland[1]	61	46	8,000	3 wks - 1 mo
McKesson[2]	63	32	10,000	N/A
Chem-Central[3]	31	25	10,000	1 mo
Detrex[6]	25	Drum Directly	15,000	
Thompson-Hayward	26	6	10,000	2 - 3 months

9.3 REFERENCES

1. Telecon. Sterett, R., Ashland Chemical Company, with Howle, R. H., Radian Corporation. February 7, 1985. Conversation on storage of chlorinated solvents.

2. Telecon. Eisner, D., McKesson Chemical Company, with Howle, R. H., Radian Corporation. February 7, 1985. Conversation on storage of chlorinated solvents.

3. Telecon. Trice, L., Chem-Central, with Howle, R. H., Radian Corporation. February 8, 1985. Conversation on storage of chlorinated solvents.

4. U.S. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors. Supplement 7. Research Triangle Park, North Carolina. Publication No. AP-42. August 1977.

5. Memorandum from Howle, R. to D. A. Beck, EPA. February 19, 1985. Distribution of Methylene Chloride, Trichloroethylene, and Perchloroethylene.

6. Telecon. Roberts, M., Detrex Chemical Industries, Inc. with Howle, R. H., Radian Corporation. February 12, 1985. Conversation on storage of halogenated solvents.

7. Telecon. Hart, W., Thompson-Hayward, with Howle, R. H., Radian Corporation. February 18, 1985. Conversation on storage of halogenated solvents.

10.0 ADDITIONAL EMISSION SOURCES OF MC

About 138,000 Mg of methylene chloride (MC) were consumed in 1983 in various uses including aerosol products, paint removers, photographic film processing, the food processing industry, and general miscellaneous applications. No attempt was made in this study to identify individual emission points for each use. However, several of these uses of MC result in emissions from the industrial point sources as well as from end use by the consumer. In general, the entire amount of MC used in these applications is emitted to the atmosphere. Table 10-1 identifies the amount of MC consumed and emitted in these additional source categories.

10.1 AEROSOLS

Methylene chloride is used as a solvent in aerosol products including finishes and coatings, hair sprays, cleaners, room deodorants, and various household and personal products. Approximately 52,900 Mg of MC were consumed in aerosol products in 1983.[1]

Aerosols are largely consumer products, although they are also used in industrial applications. Methylene chloride emissions from consumption of aerosol products result from the volatilization of suspended droplets or by evaporation from sprayed surfaces. Due to the nature of the use of aerosol products all MC in aerosol products (52,900 Mg in 1983) is emitted.

Emissions also occur at aerosol packaging plants due to spills and from evaporation during mixing and aerosol can charging.[2] It was outside of the scope of this study to investigate the amount of MC emitted at aerosol packaging facilities. However, those emissions are believed to be small relative to the total amount emitted nationwide from aerosol consumption.[2]

TABLE 10-1. ADDITIONAL USES OF METHYLENE CHLORIDE IN 1983

Source	Consumption/ Emissions (Mg/Yr)
Aerosols	52,900
Paint Removers	62,000
Photographic (film processing)	8,100
Food Processing	3,300
Miscellaneous	12,100

10.2 PAINT REMOVERS

Methylene chloride is used as a solvent in paint removers. The solvent is the primary ingredient in stripping formulations and acts to penetrate, soften, or dissolve the paint, film, or coating. Approximately 62,000 Mg of MC were consumed in paint removers in 1983.[1]

Paint removers, like aerosols, are used by both industry and consumers. The stripping formulation is applied to a painted surface and allowed to penetrate or dissolve the coating. The surface is then cleaned and the paint remnants are disposed. Emissions occur during application, use, and disposal of the removed coating. Due to the nature of the use of paint removers, all MC used in paint removers is eventually emitted to the atmosphere.

Methylene chloride is also emitted at paint remover formulation facilities. Emissions result from evaporation during mixing, packaging, and storage. These emission levels are believed to be low relative to the total amount of MC emitted nationwide from use of paint removers.[2]

10.3 PHOTOGRAPHIC FILM PROCESSING

Methylene chloride serves as a solvent in the glue used to splice film. Since the MC evaporates soon after application, emissions are assumed to be 100 percent of consumption. Total consumption and therefore emissions, of MC from splicing glue was 8,100 Mg in 1983.[1]

10.4 FOOD PROCESSING INDUSTRY

Methylene chloride consumption in the food processing industry was 3,300 Mg in 1983.[1] It is used as an extraction solvent in the extraction of heat sensitive substances such as caffeine, cocoa, and edible fats.[3] Specific emission sources were not identified in this study. However, major emission sources would most likely be in the extraction process and storage and handling facilities. In this study it was assumed that the entire 3,300 Mg consumed in the food processing industry in 1983 was emitted.

10.5 GENERAL MISCELLANEOUS

Approximately 12,100 Mg/yr of MC are consumed through miscellaneous end uses.[1] Examples of miscellaneous methylene chloride uses include use in the printing industry as a solvent for cleaning ink from printing equipment and as a thinning agent in some ink formations. It is also used to bond pieces of plastic together by dissolving the plastic at the interface of two pieces. After MC evaporation the pieces are "welded" together. Other uses for methylene chloride include use as a thinning agent for adhesives, and as a cleaner or in cleaning solutions. Emissions from these general miscellaneous categories are from evaporation during use. Additionally, MC may be used as a solvent or reactant in the chemical processing industry by companies not discussed in the chapter discussing chemical plants using MC in production (Chapter 3). The magnitude of MC use in these individual miscellaneous applications is not known at present. In addition, other small unknown uses of MC may also exist.

10.6 REFERENCES

1. Letter from D. L. Morgan, Cleary, Gottlieb, Steen, and Hamilton, to R. E. Rosensteel, EPA:ESED. March 8, 1985. Response for Halogenated Solvents Industry Alliance (HSIA).

2. PEI Associates, Inc. Occupational Exposure and Environmental Release Assessment of Methylene chloride. Prepared for the U. S. Environmental Protection Agency. Washington, D. C. (Contract No. 68-02-3935). April 1985.

3. Mannsville Chemical Products. Chemical Products Synopsis - Methylene chloride. Cortland, New York. 1984.

APPENDIX A

METHODS USED FOR ESTIMATING STORAGE TANKS AND EQUIPMENT LEAK EMISSIONS

A.1 EMISSION FACTORS FOR FIXED-ROOF STORAGE TANKS

A.1.1 Emission Equations

The major types of emissions from fixed-roof storage tanks are breathing and working losses. Emission equations for breathing and working losses from storage tanks were developed in EPA Publication No. AP-42. The equations used in estimating emissions rates for fixed-roof tanks storing VOL are:

- $L_T = L_B + L_W$
- $L_B = 1.02 \times 10^{-5} M_v \left(\frac{P}{14.7-P}\right)^{0.68} D^{1.73} H^{0.51} T^{0.5} F_p C K_c$
- $L_W = 1.09 \times 10^{-8} M_v P V N K_n K_c$

where, L_T = total loss (Mg/yr)
L_B = breathing loss (Mg/yr)
L_W = working loss (Mg/yr)

A.1.2 Parameter Values and Assumptions

The following MC physical property values, plant-specific information, and engineering assumptions were used to estimate the emission losses:

M_v = molecular weight of product vapor (lb/lb mole);
for MC, M_v = 84.93
P = true vapor pressure of product, function of temperature.
D = tank diameter (ft); dependent upon plant-specific information.
C = tank diameter factor (dimensionless):
for diameter $\geq$ 30 feet, C = 1
for diameter < 30 feet, $C = 0.0771\ D - 0.0013(D)^2 - 0.1334$
V = tank capacity (gal); dependent upon plant-specific information
N = number of turnovers per year (dimensionless); dependent upon plant-specific information

T = average diurnal temperature change in °F; diurnal temperature change assumptions were plant specific according to location

F_p = paint factor (dimensionless); the storage tanks were assumed to be in good condition and painted white; therefore, $F_p = 1$ (see Table A-1)

H = average vapor space height (ft): used tank-specific values or an assumed value of one-half the tank height (H/2)

K_C = product factor (dimensionless) = 1.0 for VOL

K_n = turnover factor (dimensionless); dependent upon plant-specific information

for turnovers > 36, $K_n = \frac{180 + N}{6N}$

for turnovers $\leq$ 36, $K_n = 1$

A.1.3 Sample Calculation

The following sample calculation is provided to demonstrate the evaluation of emissions from a typical fixed-roof storage tank containing MC. For the general equations,

$$L_T = L_W + L_B$$

$$L_B = 1.02 \times 10^{-5} M_V \left(\frac{P}{14.7-P}\right)^{0.68} D^{1.73} H^{0.51} T^{0.5} F_p C K_C$$

$$L_W = 1.09 \times 10^{-8} M_V PVNK_nK_C$$

where, $M_V = 84.93$

P = 6.75 psia (68°F)

D = 37 ft

$C = 1$

V = 233,000 gallons

$N = 10$

T = 20°F

$F_p = 1.0$

H = 14 ft

$K_C = 1.0$

$K_n = 1$

TABLE A-1. PAINT FACTORS FOR FIXED-ROOF TANKS[1]

Tank Color		Paint factors (F_p) Paint condition	
Roof	Shell	Good	Poor
White	White	1.00	1.15
Aluminum (specular)	White	1.04	1.18
White	Aluminum (specular)	1.16	1.24
Aluminum (specular)	Aluminum (specular)	1.20	1.29
White	Aluminum (diffuse)	1.30	1.38
Aluminum (diffuse)	Aluminum (diffuse)	1.39	1.46
White	Gray	1.30	1.38
Light gray	Light gray	1.33	1.44
Medium gray	Medium gray	1.40	1.58

the emissions from this storage tank are:

$$L_B = 1.02 \times 10^{-5} (84.93)\left(\frac{6.75}{14.7-6.75}\right)^{0.68} (37)^{1.73}(14)^{0.51}(20)^{0.5}(1)(1)(1)$$

$$= 6.877 \text{ Mg/yr}$$

$$L_w = 1.09 \times 10^{-8} (84.93)(6.75)(233{,}000)(10)(1)(1)$$

$$= 14.560 \text{ Mg/yr}$$

$$L_T = 6.877 \text{ Mg/yr} + 14.560 \text{ Mg/yr} = 21.44 \text{ Mg/yr}$$

A.2 EMISSION FACTORS FOR INTERNAL FLOATING ROOF STORAGE TANKS

A.2.1 Emission Equations

Emissions from internal floating roof tanks can be estimated from the following equations:[1] (Note that these equations apply only to freely vented internal floating roof tanks.)

$$L_T = L_w + L_r + L_f + L_d$$

where, L_T = the total loss (Mg/yr)

L_w = the working loss (Mg/yr) = $\frac{(0.943)\ Q\ C\ W_L}{D}\left[1 + \left(\frac{N_c F_c}{D}\right)\right]/2205$

where, D = tank diameter (ft)

N_c = number of columns (dimensionless); (see Table A-2)

F_c = effective column diameter (ft); 1.0 assumed

L_r = the rim seal loss (Mg/yr) = $(K_r D)\ P^*\ M_v\ K_C/2205$

L_f = the fitting loss (Mg/yr) = $(F_f)\ P^*\ M_v\ K_C/2205$

L_d = the deck seam loss (Mg/yr) = $(F_d\ K_d\ D^2)\ P^*\ M_v\ K_C/2205$

A.2.2 Parameter Values and Assumptions

The assumptions and values used to calculate emissions from internal floating roof tanks are:

Q = product average throughput (bbl/yr); tank capacity (bbl/turnover) x turnovers/yr; dependent upon plant-specific information

TABLE A-2. TYPICAL NUMBER OF COLUMNS AS A FUNCTION OF TANK DIAMETERS

Tank Diameter Range D (Ft)			
Greater Than	And	Less Than Or Equal To	Typical Number Columns, N_c
0		85	1
85		100	6
100		120	7
120		135	8
135		150	9
150		170	16
170		190	19
190		220	22
220		235	31
235		270	37
270		275	43
275		290	49
290		330	61
330		360	71
360		400	81

C = product withdrawal shell clingage factor ($bbl/10^3\ ft^2$); use 0.0015 $bbl/10^3\ ft^2$ for VOL in a welded steel tank with light rust (0.0075 for dense rust)

W_L = density of product (lb/gal); for MC, 11.1 lb/gal

D = tank diameter (ft)

N_c = number of columns (dimensionless); (see Table A-2)

F_c = effective column diameter (ft); 1.0 assumed

D = the tank diameter (ft); dependent upon plant-specific information

M_v = the average molecular weight of the product vapor (lb/lb mole). For MC, $M_v = 84.93$

K_c = the product factor (dimensionless) = 1.0 for VOL

2205 = constant (lb/Mg)

P^* = the vapor pressure function (dimensionless)

$P^* = 0.068\ P/((1 + (1 - 0.068\ P)^{0.5})^2)$

P = the true vapor pressure of the material stored (6.75 psia for MC)

K_r = the rim seal loss factor (lb mole/ft yr) that for an average fitting seal is as follows:

Seal system description	K_r (lb mole/ft yr)
Vapor-mounted primary seal only	6.7
Liquid-mounted primary seal only	3.0
Vapor-mounted primary seal plus secondary seal	2.5
Liquid-mounted primary seal plus secondary seal	1.6

F_f = the total deck fitting loss factor (lb mole/yr)

$$= \sum_{i=1}^{n} (N_{f_i} K_{f_i}) = [(N_{f_1} K_{f_1}) + (N_{f_2} K_{f_2}) + \ldots + (N_{f_n} K_{f_n})]$$

where, N_{f_i} = number of fittings of a particular type (dimensionless). N_{f_i} is determined for the specific tank or estimated from Tables A-2 and A-3. The values used for these emissions estimates are designated by * in Table A-3.

K_{f_i} = deck fitting loss factor for a particular type fitting (lb mole/yr). K_{f_i} is determined for each fitting type from Table A-3. The values used for these emissions estimates are designated by *.

n = number of different types of fittings (dimensionless)

F_d = the deck seam length factor (ft/ft²)

= 0.15, for a deck constructed from continuous metal sheets with a 7 ft spacing between seams

= 0.33, for a deck constructed from rectangular panels 5 ft by 7.5 ft

= 0.20, an approximate value for use when no construction details are known

K_d = the deck seam loss factor (lb mole/ft yr)

= 0.34 for nonwelded roofs

= 0 for welded decks

A.2.3 Sample Calculation

The following sample calculation is provided to demonstrate the evaluation of emissions from a typical storage tank with an internal floating roof containing MC. For the general equations,

$$L_T = L_W + L_r + L_f + L_d$$

$$L_W = \frac{(0.943)QCW_L}{D}\left[1 + \frac{N_C F_C}{D}\right]/2205$$

$$L_r = (K_r D)\ P^*\ M_V\ K_C/2205$$

TABLE A-3. SUMMARY OF DECK FITTING LOSS FACTORS (K_f) AND TYPICAL NUMBER OF FITTINGS (N_f)

Deck Fitting Type	Deck Fitting Loss Factor, K_f (lb mole/yr)	Typical Number Of Fittings (N_f)
1. Access Hatch		
A. Bolted cover, gasketed	1.6	1
B. Unbolted cover, gasketed	11 *	
C. Unbolted cover, ungasketed	25	
2. Automatic Gauge Float Well		
A. Bolted cover, gasketed	5.1	1
B. Unbolted cover, gasketed	15 *	
C. Unbolted cover, ungasketed	28	
3. Column Well		(see Table A-2)
A. Built-up column-sliding cover, gasketed	33	
B. Built-up column-sliding cover, ungasketed	47	
C. Pipe column-flexible fabric sleeve seal	10	
D. Pipe column-sliding fabric gasketed	19 *	
E. Pipe column-sliding cover, ungasketed	32	
4. Ladder Well		1
A. Sliding cover, gasketed	56 *	
B. Sliding cover, ungasketed	76	
5. Roof Leg or Hanger Well		
A. Adjustable	7.9 *	$\left(5 + \frac{D}{10} + \frac{D^2}{600}\right)$[a]
B. Fixed	0	
6. Sample Pipe or Well		1
A. Slotted pipe-sliding cover, gasketed	44 *	
B. Slotted pipe-sliding cover, ungasketed	57	
C. Sample well-slit fabric seal, 10% open area	12	
7. Stub Drain, 1-inch diameter	1.2 *	$\left(\frac{D^2}{125}\right)$[b]
8. Vacuum Breaker		1
A. Weighted mechanical actuation, gasketed	0.7 *	
B. Weighted mechanical actuation, ungasketed	0.9	

$L_f = (F_f)\ P^*\ M_v\ K_c/2205$

$L_D = (F_d K_d D^2)\ P^*\ M_v\ K_c/2205$

where, $M_v = 84.93$ lb/lb mole

$P^* = 0.152$

$Q = 500{,}000$ bbl/yr

$C = 0.0015$

$W_L = 11.1$ lb/gal

$D = 30$ ft

$N_c = 1$

$F_c = 1.0$

$K_r = 6.7$ lb mole/ft yr

$K_c = 1.0$

$F_f = 242$ lb mole yr

$F_d = 0.20$

$K_d = 0.34$

the emissions from this storage tank are:

$$L_W = \left[\frac{(0.943)(500{,}000)(0.0015)(12.3)}{30} \left(1 + \frac{(1)(1)}{30}\right) \right] /2205$$

$$= 0.123 \text{ Mg/yr}$$

$$L_r = ((6.7)(30))(0.152)(84.93)(1.0)/2205$$

$$= 1.177 \text{ Mg/yr}$$

$$L_f = (242)(0.152)(84.93)(1.0)/2205$$

$$= 1.417 \text{ Mg/yr}$$

$$L_D = ((0.20)(0.34)(30)^2)(0.152)(84.93)(1.0)/2205$$

$$= 0.358 \text{ Mg/yr}$$

$$L_T = 0.123 \text{ Mg/yr} + 1.177 \text{ Mg/yr} + 0.417 \text{ Mg/yr} + 0.358\text{Mg/yr}$$

$$L_T = 3.08 \text{ Mg/yr}$$

A.3 EQUIPMENT LEAK EMISSIONS - SAMPLE CALCULATIONS

Emissions were estimated from the number of equipment leak sources (provided by the plant), the percentage of MC in the stream (provided by the plant), and the emission factors for each type of equipment (from the SOCMI AID).[2] The following sample calculations illustrate the procedure.

Emissions Source	Number		% MC Service		Mg/yr source Emission Factor[a]		Total Emissions Mg/yr
Pump seals	3	x	7.5	x	0.0494	=	0.011
	6	x	50.5	x	0.0494	=	0.150
	2	x	87.5	x	0.0494	=	0.086
	12	x	100.0	x	0.0494	=	0.593

Emissions Source	Number		% MC Service		Mg/yr source Emission Factor[a]		Total Emissions Mg/yr
Compressors	1	x	87.5	x	0.228	=	0.200
Flanges	4	x	5.0	x	0.00083	=	0.0002
	112	x	7.5	x	0.00083	=	0.007
	30	x	18.0	x	0.00083	=	0.004
	235	x	50.5	x	0.00083	=	0.099
	66	x	87.5	x	0.00083	=	0.048
	456	x	100.0	x	0.00083	=	0.378
Valves (gas)	4	x	5.0	x	0.0056	=	0.001
	8	x	7.5	x	0.0056	=	0.003
	3	x	50.5	x	0.0056	=	0.008
	4	x	87.5	x	0.0056	=	0.020
	11	x	100.0	x	0.0056	=	0.062
Valves (liquid)	5	x	5.0	x	0.0071	=	0.002
	3	x	7.5	x	0.0071	=	0.002
	8	x	87.5	x	0.0071	=	0.050
	9	x	100.0	x	0.0071	=	0.064
Pressure Relief Devices	2	x	5.0	x	0.1042	=	0.01
	4	x	50.5	x	0.1042	=	0.21
	6	x	100.0	x	0.1042	=	0.63
Sampling Connections	5	x	5.0	x	0.0150	=	0.004
	3	x	50.5	x	0.0150	=	0.023
	1	x	87.5	x	0.0150	=	0.013
	3	x	100.0	x	0.0150	=	0.045
Open Ended Lines	1	x	100.0	x	0.0017	=	0.002
					TOTAL	=	2.7252

Annual Emissions = 2.72 kg/hr x 8760 hrs/year x Mg/1,000 kg

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[a] U. S. Environmental Protection Agency. Fugitive Emission Sources of Organic Compounds - Additional Information on Emissions, Emission Reductions, and Costs. Research Triangle Park, NC. Publication No. EPA-450/3-82-010. April 1982.

A.4 REFERENCES

1. U. S. Environmental Protection Agency. VOC Emissions from Volatile Organic Liquid Storage Tanks - Background Information for Proposed Standards. Research Triangle Park, North Carolina. Publication No. EPA-450/3-81-003a. July 1984. 252 pp.

2. U.S. Environmental Protection Agency. Fugitive Emission Sources of Organic Compounds - Additional Information on Emissions, Emission Reductions, and Costs. Research Triangle Park, N.C. Publication No. EPA-450/3-82-010. April 1982.

APPENDIX B

METHODS FOR ESTIMATING EMISSION CONTROL COSTS

B.1 PROCESS VENT EMISSIONS CONTROL COST ESTIMATION

The cost estimates for process vent emission control are based on the use of thermal incineration. The procedure for estimating these costs uses the methods presented in the Air Oxidation Processes Control Techniques Guidelines (CTG) document.[1] A detailed discussion of the incinerator costing methods may be found in Chapter 5 of this document. It should be noted that these incinerator costing procedures are designed for vent streams having high flowrates. Since the vent streams containing MC generally have lower flowrates, the cost estimates for process vent emission control may be somewhat overstated. Further work will be performed to develop incinerator costing procedures for lower flowrate vent streams if regulatory development proceeds.

The total installed capital cost of control is determined using the following equation:

Total Installed Capital Cost (10^3\$) = (# of incinerators) x (escalation factor) x (C1 - (Waste Heat Boiler Correction Factor) + (C2 x (Flowrate per incinerator Design Vent Size Factor)^{C3}) + (pipe rack cost) + (additional ductwork cost)

where: C1, C2, and C3 are coefficients from Table B-1 that depend upon heating value and halogenation status of a given vent stream; waste heat boiler correction factor of 40 (10^3\$) is used for vent streams with flowrates below 700 scfm, where no heat recovery in a waste heat boiler is assumed; escalation factor of 0.90 deescalates costs to 1978 dollars;

design vent size factor of 0.95 increases vent stream flowrate for costing purposes;

pipe rack cost is calculated using the equation presented in Table B-2;

additional ductwork cost is calculated using the equation presented in Table B-3.

TABLE B-1. TOTAL INSTALLED CAPITAL COST AS A FUNCTION OF VENT STREAM FLOW RATE

Category	Maximum Flowrate Per Unit (10^3 scm/min)	Minimum Net Heating Value (MJ/scm)	Maximum Net Heating Value (MJ/scm)	Fabricated Equipment Cost Escalation Factor	C1	C2	C3
A1[a]	0.74	0.0	3.5	0.90	803.11	12.83	0.88
A2[a]	0.74	3.5	-	0.90	786.61	12.44	0.88
B	1.42	0.0	0.48	0.90	259.88	4.91	0.88
C	1.42	0.48	1.9	0.90	297.99	2.84	0.88
D	1.25	1.9	3.6	0.90	236.35	3.23	0.88
E[a]	1.25	3.6	-	0.90	236.35	3.23	0.88

[a] Halogenated vent stream.

[b] Dilution flow rate is used in capital cost equation. Dilution flow rate = (design flow rate) x (original heating value) ÷ (3.65 MJ/scm).

TABLE B-2. ADDITIONAL DUCT COST[1,2]

Additional duct cost (10^3 $) = (length) x (cost per unit length) x (installation factor) x (duct escalation factor) x (retrofit correction factor) ÷ 1000

Cost per unit length = 1.37L - 1.76

where L = duct diameter in inches

$$\text{Diameter} = \left[\frac{\text{Flow rate (ft}^3\text{/min)}}{\text{Linear velocity (ft/min)}} \times \frac{4}{\pi} \right]^{0.5}$$

$$= \left[\frac{\text{Flow rate (ft}^3\text{/min)}}{2000 \text{ ft/min}} \times \frac{4}{3.1412} \right]^{0.5}$$

if linear velocity is assumed to be 2000 ft/min

Additional duct length = 150 ft + (additional vents x 100 ft/vent)

Installation factor = 1.087

Escalation factor (from 1977 to 1978) = 1.088

Retrofit correction factor = 1.0

TABLE B-3. PIPE RACK COST[1,2]

Pipe rack cost (10^3 \$) = (pipe rack length) x (cost per unit length) x (installation factor) x (pipe rack escalation factor) x (retrofit correction factor) ÷ 1000

Pipe rack length = 250 ft + (# additional vents x 100 ft/vent)

Cost per unit length = \$32.045/ft

Installation factor = 1.087

Deescalation factor (1982 to 1978) = 0.746

Retrofit correction factor = 1.0

TABLE B-4. OPERATING FACTORS FOR EACH DESIGN CATEGORY

Category	Minimum Net Heating Value (MJ/scm)	Maximum Net Heating Value (MJ/scm)	Ratio of Flue Gas Flow to Offgas Flow[a]	Heat Recovery Factor (MJ/scm)	Pressure Drop (Inches H_2O)	Natural Gas Use Coefficients G0	G1	G2	G3
A1[b]	0	3.5	2.9	3.38	22[c]	0	4.56	-0.985	0
A2[b]	3.5	-	2.9	3.38	22[c]	0	0.329	0	0
B	0.	0.48	1.9	0	10[d]	0.425	0.666	-1.29	0.015
C	0.48	1.9	2.3	0	10[d]	0	2.39	-1.22	0
D	1.9	3.6	2.5	0	6[e]	0	0.183	0	0
E	3.6	-	2.5	0	6[e]	0	0.183	0	0

[a] Both at standard conditions.

[b] Offgas contains halogenated compounds.

[c] Includes 6 inches across the combustion chamber, 4 inches across the waste heat boiler, and 12 inches across the scrubber.

[d] Includes 6 inches across the combustion chamber and 4 inches across the recuperative heat exchanger.

[e] Across the combustion chamber.

TABLE B-5. ANNUALIZED COST FACTORS

All Factors are Based on June 1980

Direct

Operating Labor: \$8.50/hr (Includes Overhead)
Operating Labor Factor: 2400 Man-hr/yr (Categories A1-A2)
2133 Man-hr/yr (Categories B-C)
1200 Man-hr/yr (Categories D-E)

Supervisory Labor: \$8.50/hr x (0.15)

Total Labor: [(\$8.50/hr x 1.15) + (0.03 of Total Installed Capital)]

Overhead Labor: 0.80 of Total Labor
Electricity: \$0.0279/kWh
Natural Gas: \$4.16/GJ =
Heat Recovery Credit: \$4.16/GJ =
Quench Water Price: \$0.22/Thousand Gallons
Scrubbing Water Price: \$0.22/Thousand Gallons
Caustic Price: \$0.0436/lb[a]
Maintenance Labor Plus Materials Factor = 0.06 of Total Installed Capital

Indirect ("Capital Charges")

Interest Rate = i = 10%

Incinerator Lifetime = 10 Years = N

Capital Recovery Factor = $\frac{i\,(1 + i)^N}{(1 + i)^N - 1}$

= 0.163 of Total Installed Capital

Taxes, Insurance and Administrative Charges Factor = 0.04 of Total Installed Capital

Overall Capital Charges Factor = 0.203 of Total Installed Capital

Overall Taxes and Maintenance Factor = 0.10 of Total Installed Capital

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[a] Fifty percent liquid solution of caustic soda.

[b] Memo to Hurley, E., EEA, from Galloway, J., EEA. January 13, 1981. Average capacity utilization for the air oxidation industry.

TABLE B-6. SAMPLE CALCULATION FOR INCINERATOR COSTING

1. Capital Cost (10^3 \$)	= (# incinerators) x (incinerator capital cost per unit) x (escalation factor) = (# incinerators) x (803.11 - 40.0 + 12.83 x $(\text{flow}/0.95)^{0.88}$) x escalation factor = 1 x (803.11 - 40.0 + 12.83 $(14.2)^{0.88}$) x 0.9 = 806.1
2. Additional Duct Cost (10^3 \$)	= (length) x (cost per unit length) x (escalation factor) x (installation factor) = 350 ft. x $((((500\ \text{ft}^3/\text{min}) \times 4 \div 2000 \div 3.1412))^{0.5} \times 12 \times 1.37 \div 1.76) \times 1.088 \times 1.087 \div 1000$ = 3.111
3. Pipe Rack Cost (10^3 \$)	= (length) x (cost per unit length) x (installation factor) x (pipe rack escalation factor) x (retrofit correction factor) ÷ 1000 = 250 ft. + (2 additional vents x 100 ft./vent) x \$32.045/ft. x 1.087 x 0.746 x 1.0 ÷ 1000 = 11.693
4. Total Installed Total Capital	= Capital cost (10^3 \$) + extra duct cost (10^3 \$) + pipe rack cost (10^3 \$) = 806.1 + 3.111 + 11.693 = 820.9

(continued)

TABLE B-6. (Continued)

5. Natural Gas Use (MJ/yr)
= (minutes per year) x (supplemental gas required per minute)
= 0.5256 10^6 min/yr x G_0 + flow x (G_1 + G_2 x H_T)
= 0.5256 10^6 min/yr x (3.96) x (4.53 - 0.985 x 1.49) MJ/min)
= 6.37 MJ/yr

6. Natural Gas Cost (10^3 \$)
= Natural gas price (\$/10^9 J) x natural gas use (MJ/yr)
= \$4.16/GJ x 6.37 MJ
= 26.2

7. Operating Labor Cost (10^3 \$)
= Wage (\$/hr) x labor factor (hr/yr) ÷ 1000
= \$8.50/hr x 2400 hrs
= 20.4

8. Supervisory Labor Cost (10^3 \$)
= Operating labor cost (10^3/yr) x 0.15
= 20.4 (10^3 \$/yr) x 0.15
= 3.06

9. Maintenance Labor Cost (10^3 \$)
= Installed capital cost (10^3 \$) x 0.03
= 820.9 (10^3) \$ x 0.03
= 24.63

10. Overhead Labor Cost (10^3 \$)
= Operating labor cost (10^3 \$) + supervisory labor cost (10^3 \$) + maintenance labor cost (10^3 \$) x 0.80
= (20.40 + 3.06 + 24.63) x 0.80
= 38.47

(continued)

TABLE B-6. (Continued)

11. Total Labor Cost $(10^3\ \$)$	= Operating labor cost $(10^3\ \$)$ + supervisory labor cost $(10^3\ \$)$ + maintenance labor cost $(10^3\ \$)$ + overhead labor cost $(10^3\ \$)$ = 20.4 + 3.06 + 24.63 + 38.47 = 86.56
12. Electricity Cost $(10^3\ \$)$	= (electricity price) x (pressure drop) x (flow rate) x (flue gas:offgas ratio) x (fan equation conversion factor) x (# of hours per year) ÷ fan efficiency ÷ 1000 = 0.0279 $(\$/\mathrm{KWhr})$ x 22 in. x 3.96 scm/min x 2.9 x 0.004136 (KW/scmin.) ÷ 0.6 ÷ 1000 $(\$/10^3\ \$)$ = 0.426
13. Quench Water Cost $(10^3\ \$)$	= (quench water price) x (flow rate) x (flue gas:offgas ratio) x (water required per unit flow) x (minutes per year) ÷ 1000 = 0.22 $(\$\ 10^3$ gal) x 3.96 (scm/min) x 2.9 x 1.68×10^{-5} $(10^3$ gal/scm) x 0.5256 $(10^6$ min/yr) ÷ 1000 $(\$/10^3\ \$)$ = 0.0223

(continued)

TABLE B-6. (Continued)

14. Scrubbing Water Cost (10^3 $)	= (scrub water price) x (flow rate) x (flue gas:offgas ratio) x (chlorine content of flue gas) x (water required per unit chlorine) x (# of hours per year) = 0.22 ($$10^3$ gal) x 3.96 (scm/min) x 35.314 scf/scm x 2.9 x 0.0487 (lb/hr chlorine)/(scf/min flue gas) x 0.0192 (10^3 gal/lb chlorine) x 8760 (hr/yr) ÷ 1000 = 0.73
15. Neutralization Cost (10^3 $)	= (caustic cost) x (flow rate) x (flue gas:offgas ratio) x (chlorine content of flue gas) x (caustic requirement per unit chlorine) x (# of hours per year) ÷ 1000 = 0.0436 ($/lb NaOH) x 3.96 (scm/min) x 35.314 scf/scm x 2.9 x 0.0487 (lb/hr chlorine)/(scf/min flue gas) x 1.14 (lb NaOH/lb chlorine) x 8760 (hr/yr) ÷ 1000 = 8.6
16. Heat Recovery Credit	= 0 (for all streams <700 scfm)

(continued)

TABLE B-6. (Continued)

17. Taxes, Insurance, and Maintenance Cost (10^3 \$) = (installed capital cost) x (taxes, insurance, and administrative charges factor + maintenance labor factor)
= 820.9 (10^3 \$) x (0.04 + 0.03)
= 57.46

18. Annual Operating Cost (10^3 \$) = (TI&M cost) + (gas cost) + total labor cost) + (electricity cost) + (quench cost) + (scrubbing cost) + (scrubbing cost) + (caustic cost)
= 57.46 + 26.20 + 86.56 + 0.426 + 0.0223 + 0.73 + 8.6
= 180.90

19. Annualized Cost (10^3 \$) = (operating cost) + (capital recovery factor x total installed capital cost)
= 180.0 + (.163 x 820.9)
= 313.8

20. Annual Emissions (Mg/yr) = (hourly emissions) x 365 (days/yr) x 24 (hrs/day) x (Mg/10^3 kg)
= 15.86 kg/hr x 365 (days/yr) x 24 (hrs/day) x 1 (Mg/10^3 kg)
= 138.9

21. Annual Emission Reduction (Mg/yr) = (annual emissions) x 0.98
= 138.9 x 0.98 (MC) = 136.1 (MC)
= 349.6 (VOC)

(continued)

TABLE B-6. (Continued)

22. Cost Effectiveness ($/Mg)	= (annual cost) ÷ (annual emission reduction) = 313.8 (10^3 $) ÷ 136.1 Mg (MC = 2305/Mg (MC) = 313.8 (10^3 $) ÷ 349.6 Mg (VOC) = $898/Mg
23. Updated Cost-Effectiveness Values ($/Mg)	= 2305 ($/Mg) x 1.486 = $3420/Mg (MC) = 898 ($/Mg) x 1.486 = $1330/Mg (VOC)

TABLE B-7. COST CONVERSION FACTORS FOR INCINERATOR COMPONENTS

Original Cost Component	Original Conversion Year	Conversion Year	Conversion Factor
Incinerator	1979	1978	0.900
Pipe Rack	1982	1978	0.745
Duct Work	1977	1978	1.088
Annualized Costs	1978	1984	1.486

A sample calculation for incinerator costing is shown in Table B-6. The calculation is based on representative vent stream parameters for a typical MC production facility. The cost estimate was initially calculated in 1978 dollars and then was updated to 1984 dollars using the annualized cost escalation factor shown in Table B-7.

B.2 COST CALCULATIONS FOR INSTALLING INTERNAL FLOATING ROOFS IN FIXED ROOF TANKS

The following equations were used to calculate the capital and annualized cost for the installation of a mild steel welded contact internal floating roof to a fixed roof storge tank. This internal floating roof utilizes both primary (constructed of Teflon^R) and secondary (constructed of Viton^R) seals.

B.2.1 Capital Cost (4th Quarter 1982 Dollars)

1. Degassing Cost[4]

Cost = \$130.8 $V^{0.5132}$ or \$1,000, whichever is greater where V = tank volume in cubic meters.

2. Estimated Installation Cost[4]

   a. Basic cost of roof and primary seal:
   Cost = (1.91 + 2.54 x D) x \$1,000 + (\$204 x D)
   D = tank diameter in meters

(The \$204 x D cost reflects the additional cost of using Teflon^R coated fiberglass to protect against MC attack versus the standard polyurethane coating)[5]

   b. Additional cost of adding secondary seal:[4]

   Cost = \$580 x D

(The \$580 x D cost reflects using a Viton^R coating material for the secondary seal)

3. Door Sheet Opening Cost[6]

   Cost = \$1,300

Total capital cost (primary seal) = degassing cost + estimated installed cost (2a) + door sheet opening cost.

Total capital cost (primary + secondary seals) = degassing costs + estimated installed cost (2a,b) + door sheet opening cost.

B.2.2 Annual Cost (4th Quarter 1982 Dollars)

1. Taxes, insurance, and administration -- 4% of capital cost (based on 10 percent interest rate and 10 year equipment life)
2. Maintenance -- 5% of capital cost
3. Inspection -- 1% of capital cost
4. Capital recovery factor -- 16.275% of capital cost

Total annual cost = [26.275% of capital cost]

B.2.3 MC/VOC Reduction

1. Emissions calculated for fixed roof tanks using AP-42 formulas.
2. Emissions calculated for internal floating roof tanks using AP-42 formulas.
   - a. Liquid mounted primary seal only
   - b. Liquid primary and secondary seal

3. Emissions from fixed roof tank - emissions from internal floating roof tank = VOC emission reduction

   MC emission reduction = VOC emission reduction x percentage of MC in stored material

B.2.4 Recovery Credits (4th Quarter 1984 Dollars)

Credits = (MC emission reduction) x (4th Quarter 1984 MC market value ($485/Mg)) + [(VOC emission reduction-MC emission reduction) x (4th Quarter 1984 VOC market value ($330/Mg))].

B.2.5 Net Annual Cost

Before annual cost can be calculated, all costing data is converted to 1984 dollars using Chemical Engineering Economic Indicators)

Cost = annual cost (4th quarter 1984 dollars) - VOC recovery credits (4th Quarter 1984 dollars)

B.2.6 Cost Effectiveness

MC cost effectiveness = net annual cost/MC emission reduction (Mg)

VOC cost effectiveness = net annual cost/VOC emission reduction (Mg)

B.3 COST CALCULATIONS FOR INSTALLATION OF REFRIGERATED CONDENSERS TO CONTROL STORAGE AND LOADING EMISSIONS

This section presents methods used to estimate costs for controlling storage and loading emission by condensation. Based on Section 114 letter responses, 85% control efficiency was assumed for storage applications and 90% control efficiency was assumed for loading applications.

Costs were estimated using methods in Capital and Operating Costs of Selected Air Pollution Control Systems. Based on conversation with one chloroflorocarbon producer, one carbon tetrachloride producer and Section 114 response the following assumptions were made.

Source of Stored Material	Filling Rate (gpm)	Gas Flow Rate to condenser (scfm)
Production	200	27
Ship	1800	240
Barge	800	110
Rail Car	200	27
Tank Truck	200	27

B.3.1 Capital Cost (4th Quarter 1984 Dollars)

Capital Cost (1977$) = [0.27 x Flow (scfm) + 34] x 1000[3]

Installed Cost = Capital Cost x 1.74[2]

4th Quarter 84 Installed Cost = Installed Cost x $\frac{324.4}{210.3}$

CE Index

December 77 = 210.3
November 84 = 324.4

B.3.2 Annual Cost

1. Taxes, insurance, and administration -- 4 percent of capital
2. Maintenance -- 5 percent of capital
3. Inspection -- 1 percent of capital
4. Capital Recovery Factor -- 16.275 percent of capital

Annualized capital cost = Installed capital cost x .26275

Electricity cost = [(0.35) x Flow (scfm) + 10] x kw cost

kw cost = $0.522/kw

B.3.3 MC/VOC Emission Reduction

1. Calculate fixed roof storage emission using AP-42 and storage tank data

MC emission = FR emissions x % MC in stored material
VOC emission = Total FR emissions

2. MC emission red = MC emissions x .85
VOC emission red = VOC emissions x .85

B.3.4 Recovery Credit

Credits = (MC emission reduction) x (4th Quarter 1984 MC market value
($485/MG)) + [(VOC emission reduction-MC emission reduction) x
(4th
Quarter 1984 VOC market value ($330/MG))].

B.3.5 Net Annual Cost

Net annual cost = (total annual cost) - (recovery credit)

B.3.6 Cost Effectiveness

MC C/E = Net annual cost ÷ MC emission red
VOC C/E = Net annual cost ÷ VOC emission red

B.4 SAMPLE CALCULATIONS FOR EQUIPMENT LEAK CONTROL COSTS

To calculate the cost for the implementation of technologies to control equipment leak emissions, the specific control techniques, removal efficiencies and capital/annualized costs per component are given in Table B-8. The equipment leak emission sources costed are pump seals, compressors, flanges, valves, pressure relief devices, sample connections, and open ended lines.

Capital cost per emission source: (No. of components) x (capital cost per component)

Total capital cost per plant: ÷ [capital cost per emission source] annual cost per emission source: (No. of components) x (annual cost per component)

MC emission reduction per emission source: (current MC emission) x (percent reduction)

Total MC emission reduction per plant: ÷ [MC emission reduction per emission source]

TABLE B-8. CONTROL TECHNIQUES AND COST FOR CONTROLLING EQUIPMENT LEAK EMISSION SOURCES[a]
(4th Quarter 1984 Dollars)

Equipment Type (Emission Source)	Control Techniques	Percent Reduction[5]	Capital[6] Cost $/Component	Annualized[6] Cost $/Component
1. Pump seals				
- Packed	Monthly LDAR	61	0	370
- Mechanical	Monthly LDAR	61	0	370
- Double Mechanical	N/A	N/A	N/A	N/A
2. Compressors	Vent to combustion device	100	10,200	2,580
3. Flanges	None Available	N/A	N/A	N/A
4. Valves				
- Gas	Monthly LDAR	73	0	20
- Liquid	Monthly LDAR	59	0	20
5. Pressure Relief devices				
- Gas	O-Ring	100	310	80
- Liquid	N/A	N/A	N/A	N/A
6. Sample Connections				
- Gas	Closed-purge sampling systems	100	670	170
- Liquid	Closed-purge sampling systems	100	670	170
7. Open Ended Lines				
- Gas	Caps on open ends	100	70	20
- Liquid	Caps on open ends	100	70	20

[a] Updated to 4th quarter 1984 using CE index.

VOC emission reduction per emission source: (current VOC emission) x (percent reduction)

Total VOC emission reduction per plant: ÷ [VOC emission reduction per emission source i]

Recovery credit per emission source: (MC emission reduction per source i) x (4th Quarter 1984 MC market value ($485/Mg)) + [(VOC emission reduction per source i - MC emission reduction per source i) x (4th Quarter 1984 VOC market value ($330/Mg))].

Recovery credit per plant: The summation of recovery credits per emission source.

Net annual cost (MC) per emission source: (annual cost per emission source) minus (recovery credits per emission source).

Net annual cost (MC) per plant: (total annual cost per plant) minus (total recovery credits per plant).

Net annual cost (VOC) per emission source: (annual cost per emission source) minus (recovery credits per emission source).

Net annual cost (VOC) per plant: (total annual cost per plant) minus (total recovery credits per plant).

Cost effectiveness for controlling MC emissions per emission source: (net annual cost (MC) per emission source) ÷ (MC emission reduction per emission source).

Cost effectiveness for controlling MC emissions per plant: (net annual cost (MC) per plant) ÷ (MC emission reduction per plant).

Cost effectiveness for controlling VOC emissions per emission source: (net annual cost (VOC) per emission source) ÷ (emission reduction per emission source).

Cost effectiveness for controlling VOC emissions per plant: (net annual cost (VOC) per plant) ÷ (emission reduction per plant).

B-5 REFERENCES

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5. U.S. Environmental Protection Agency. Fugitive Emission Sources of Organic Compounds - Additional Information Document. Research Triangle Park, N.C. Publication No. EPA-450/3-82-010. April 1982. p. 1-4.

6. U.S. Environmental Protection Agency. Benzene Fugitive Emissions - Background Information for Promulgated Standards. Research Triangle Park, N.C. Publication No. EPA-450/3-80-032b. June 1982. Appendix A.

APPENDIX C

SUMMARY OF EXISTING STATE AND FEDERAL REGULATIONS AFFECTING METHYLENE CHLORIDE EMISSION SOURCES

C.1 EXISTING STATE REGULATIONS

C.1.1 Introduction

Methylene chloride (MC) emissions originate from several industrial sources. These sources include producers of MC, sources that use MC as a chemical intermediate, and sources that store MC. These emissions can be characterized as either process, equipment leak, product storage tank, or loading and handling emissions.

There are a number of different regulations at the State level that limit volatile organic compound (VOC) emissions. VOC emissions in nonattainment areas (areas that have not achieved the ambient air quality standards for ozone) are normally controlled by the States' RACT program. VOC emissions in areas designated as attainment or unclassified for ozone are controlled by Prevention of Significant Deterioration (PSD) regulations. MC is excluded from many of these state regulations due to its low photochemical reactivity. However, eleven States that have regulations controlling VOC emissions do not specifically exclude MC from the applicable regulations. These States are Alabama, Kentucky, Massachusetts, Maryland, Michigan, Nevada, New Jersey, Pennsylvania, Rhode Island, Tennessee, and Wisconsin.

C.1.2 General State VOC Regulations for Solvent Use

In addition to the RACT and PSD programs, 12 States (including the District of Columbia) have general VOC regulations that limit emissions of photochemically reactive solvents. Table C-1 presents a list of the States that have adopted a general VOC solvent usage regulation and the emission limits established by each State. These regulations affect volatile organic solvents found to be photochemically reactive and usually require 85 percent reduction in VOC emissions. Methylene chloride is excluded from regulation by all of these States with the exception of Maryland and Rhode Island.

TABLE C-1. GENERAL STATE VOC REGULATIONS FOR PHOTOCHEMICAL SOLVENTS[1]

State	Emission Reduction (%)
California	85
Colorado	85
Connecticut	85
District of Columbia	85
Illinois	85
Indiana	85
Louisiana	90
Maryland	85[2]
North Carolina	85
North Dakota	85
Rhode Island	85[3]
Virginia	85

[1] These regulations exclude MC with the exception of Maryland and Rhode Island.

[2] Applies to sources in nonattainment areas only.

[3] Applies to sources emitting less than 100 tons/year, larger sources must comply with RACT.

C.1.3 Prevention of Significant Deterioration Regulations

PSD regulations control VOC emissions from major sources in areas classified as attainment for ozone. Under PSD regulations, a chemical production plant must seek a PSD permit if it is: (1) a new source with emissions or potential emissions considered major (100 tons/yr); (2) a major increase in emissions or potential emissions (100 tons/yr) at an existing minor source; or (3) a significant increase in emissions or potential emissions (40 tons/yr) at an existing major source. Emission control levels for PSD are established during the State's review of the PSD permit application prepared for the emission source.

C.1.4 State Regulations Affecting Chemical Production

In addition to the general discussion of State regulations concerning MC emission sources, a more indepth review was performed for States in which MC production facilities and facilities using MC in production are located. Only two States, Michigan and Pennsylvania, had regulations controlling MC emissions from chemical production facilities. These regulations are presented in Table C-2. All applicable MC emissions must be controlled under these regulations due to the 6.75 psia vapor pressure of MC. Other VOC emissions at these facilities may also be controlled.

C.2 EXISTING FEDERAL REGULATIONS

Several VOC NSPS and a NESHAP have been developed that could affect new and some existing sources of MC emissions. A summary and the current status of each of these standards are presented in Table C-3.

TABLE C-2. STATE REGULATIONS AFFECTING CHEMICAL PRODUCTION FACILITIES EMITTING METHYLENE CHLORIDE

State	Source	Regulation
Michigan[1]	Storage tanks >40,000 gal true vapor pressure >1.5 <11.0 (existing sources)	- Pressure tank or - Floating cover with closure seal or seals - Vapor recovery system capable of 90 percent recovery
	Storage of organic compounds having a true vapor pressure $\geq$11 psia in existing vessels of >40,000 gallons	- Pressure tank capable of maintaining working pressures sufficient to prevent organic vapor or gas loss to atmosphere - Vapor recovery system which recovers >90% by weight of uncontrolled organic vapor - All openings shall be equipped with covers, lids, or seals
	VOC loading facilities handling $\geq$5,000,000 gal/year of >1.5 psia VOC	- submerged fill pipes in ozone attainment areas
Pennsylvania[1]	Above ground storage tanks <40,000 gal and >2,000 gal true vapor pressure >1.5 psia	- Pressure tank or - External or internal floating roof is true vapor pressure $\leq$11.0 psia or - Vapor recovery system capable of 80 percent recovery
	Storage tanks $\leq$40,000 gal true vapor pressure >1.5 psia	- Pressure relief valves

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[1] Environment Reporter, State Air Laws. Washington, D. C. Bureau of National Affairs.

TABLE C-3. SUMMARY OF FEDERAL REGULATIONS AFFECTING VOLATILE ORGANIC COMPOUND EMITTING SOURCES

Source	Proposed	Promulgated
SOCMI Equipment Leaks (Fugitive) NSPS	01/05/81	10/18/83
VOL Storage Vessels NSPS	10/84	
SOCMI Air Oxidation NSPS	10/21/83	
SOCMI Distillation Operations NSPS	12/30/83	
SOCMI Reactor Processes NSPS	draft	

APPENDIX D

MATERIAL BALANCE FOR MC EMISSIONS OPERATIONS

D.1 MATERIAL BALANCE

(1) - Fraction of degreasing use of MC in cold cleaning = 0.67

Fraction of degreasing use of MC in vapor degreasing = 0.33

- Emission factors:

  - cold cleaning: 0.43 kg/kg used
  - open top degreasing: 0.78 kg/kg used
  - conveyorized degreasing: 0.85 kg/kg used

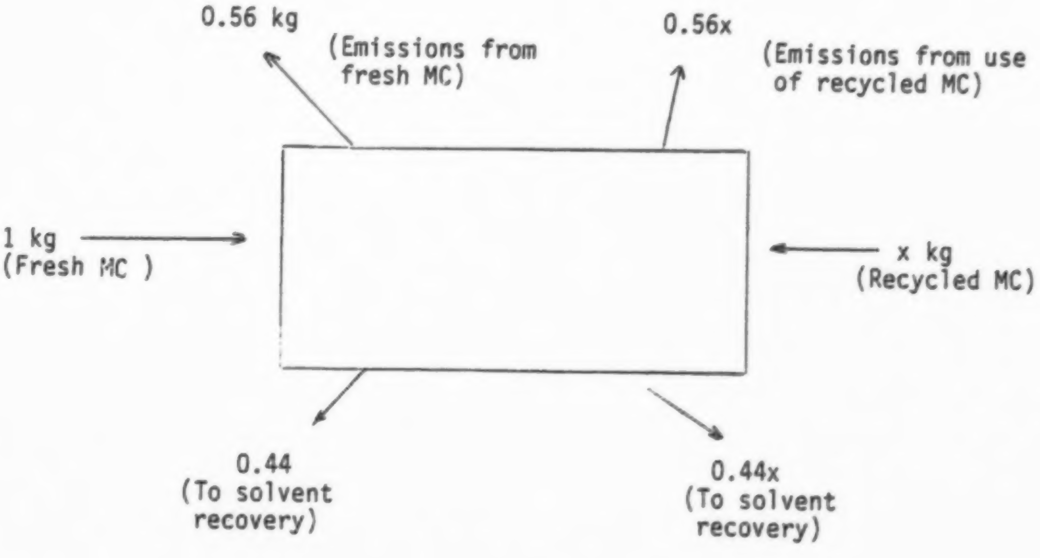
- Assuming methylene chloride usage in vapor degreasing is divided equally between open top and conveyorized vapor degreasing, a weighted average emission factor is calculated as follows:

$$(0.67)(0.43) + (0.165)(0.78) + (0.165)(0.85) = 0.56 \text{ kg/kg used}$$

(2) - For every kg of fresh MC used, 0.56 kg is emitted. Assume all of the remaining 0.44 kg is sent to solvent recovery.

- Estimate that 75 percent of all solvent sent to recovery is recycled.

- Calculate emissions as follows:


0.56 kg
(Emissions from fresh MC)
0.56x
(Emissions from use of recycled MC)
1 kg
(Fresh MC)
x kg
(Recycled MC)
0.44
(To solvent recovery)
0.44x
(To solvent recovery)

$x = 0.75\ (0.44 + 0.44x)$

$x = 0.49$ (Amount of recycled MC used per kg of fresh MC used)

$0.56x = 0.27$ (Amount of recycled MC emitted per kg of fresh MC used)

Total MC emitted per kg of fresh MC used = 0.56 + 0.27

= 0.83 kg

D.2 NATIONAL EMISSION REDUCTION CALCULATIONS

National emission reduction can be calculated by estimating the amount of solvent emitted by the degreasers that are presently uncontrolled and applying a control efficiency to these emissions. The emission factors presented in Section D.1 for cold cleaners, open top vapor degreasers, and conveyorized vapor degreasers are overall emission factors representing the average emission factor from controlled and uncontrolled degreasers. An uncontrolled degreaser emission factor was developed for the three types of degreasers so that the national emissions from uncontrolled degreasers could be calculated. An uncontrolled degreaser is considered to be one that does not have the most stringent control techniques for its degreaser type. These control techniques were described in Chapter 4. For example, the most stringent control technique for an open top vapor degreaser is a carbon adsorber. Therefore, an uncontrolled open top vapor degreaser is one that does not control emissions with a carbon adsorber. In reality, degreasers have levels of controls ranging from no control techniques to the most stringent control techniques available. Therefore, defining an uncontrolled degreaser as one that does not have the most stringent control techniques for its degreaser type results in an overestimate of the achievable emission reduction.

Information on the number of uncontrolled versus controlled degreasers was obtained from industry contacts.[1,2] These are as follows:

- Ratio of uncontrolled/controlled cold cleaners
  = 0.65/0.35
- Ratio of uncontrolled/controlled open top vapor degreasers
  = 0.99/0.01
- Ratio of uncontrolled/controlled conveyorized vapor degreasers
  = 0.95/0.05

The uncontrolled degreaser emission factors were then calculated according to the following equation:

$(a)x + (b)(c)x = y$

where:

y = overall degreaser emission factor, kg/kg solvent consumed
a = fraction of uncontrolled degreasers
x = uncontrolled degreaser emission factor, kg/kg solvent consumed
b = fraction of controlled degreasers
c = 1 - achievable emission reduction

Since emission reduction is calculated only for presently uncontrolled degreasers, the total solvent consumption must be adjusted to include only the solvent used in uncontrolled degreasers. The adjusted solvent consumption levels were calculated according to the equation:

(1) $z = (s)(t)(u)$

where:

z = total solvent consumed by uncontrolled degreasers by degreaser type, Mg/yr
s = total solvent consumption by all degreasers (fresh solvent plus recycled solvent = total emissions divided by emission factor for fresh MC), Mg/yr
t = fraction of consumption by degreaser type
u = fraction of uncontrolled degreasers by degreaser type

The uncontrolled emission factors were applied to the total amount consumed by uncontrolled sources within each degreaser type to yield the national uncontrolled emissions for the degreaser type. Applying the control efficiency to the national uncontrolled emissions gives the emission reduction for the degreaser type. These calculations proceed according to the equation:

(2) $r = (z)(x)(v)$

where:

r = emission reduction for degreaser type, Mg/yr

z = total solvent consumed by uncontrolled degreasers by degreaser type, Mg/yr

x = uncontrolled degreaser emission factor (kg/kg solvent consumed)

v = achievable emission reduction

Calculations:

I. Cold Cleaners

(1) $y = (a)x + (b)(c)x$

$0.43 = (0.65)x + (0.35)(1-0.35)x$

$x = 0.49$

(2) $z = (s)(t)(u)$

$z = \frac{17,700}{0.56}(0.67)(0.65)$

$z = 13,800$ Mg/yr

(3) $r = (z)(x)(v)$

$r = 13,800\ (0.49)(0.35)$

$r = 2,360$ Mg/yr

II. Open Top Vapor Degreasers

(1) $y = (a)x + (b)(c)x$

$0.78 = (0.99)x + (0.01)(1-0.44)x$

$x = 0.78$

(2) $z = (s)(t)(u)$

$z = \frac{17,700}{0.56}(0.165)(0.99)$

$z = 5,160$ Mg/yr

(3) $r = (z)(x)(v)$

$r = (5,160)(0.78)(0.44)$

$r = 1,770$ Mg/yr

III. Conveyorized Vapor Degreasers

(1) $y = (a)x + (b)(c)x$

$0.85 = (0.95)x + (0.05)(1-0.57)x$

$x = 0.87$

(2) $z = (s)(t)(u)$

$z = \frac{17,700}{0.56}(0.165)(0.95)$

$z = 4,950$ Mg/yr

(3) $r = (z)(x)(v)$

$r = (4,950)(0.87)(0.57)$

$r = 2,460$ Mg/yr

D.3 PHOTORESIST STRIPPING EMISSION FACTOR

1. Emission factor = 0.25 kg/kg used

2. For every kg of fresh MC used, 0.25 is emitted. Assume remaining .75 is sent to solvent recovery.

   - Estimate that 75 percent of all solvent sent to recovery is recycled

   $x = 0.75\ (0.75 + 0.75x)$

   where x = recycled solvent

   $x = 1.29$ (amount recycled MC used per kg of fresh MC used)

   $0.25x = 0.32$ (amount recycled MC emitted per kg fresh MC used)

3. Total MC emitted per kg fresh MC used

   $= 0.25 + 0.32$

   $= 0.57$

D.4 REFERENCES

1. Telecon. Murphy, P.V., Radian Corporation, with Pokorng, J., Baron-Blakeslee, Inc. August 9, 1985. Information on control devices for degreasers.

2. Telecon. Murphy, P.V., Radian Corporation, with Barr, F., Graymills Corp. August 9, 1985. Information on control devices for cold cleaners.

APPENDIX E

EMISSIONS FROM DISTRIBUTION FACILITIES

(1) Estimate the quantity going through distribution (storage)

1983 production = 530 MM lbs

Assume 100 percent goes through distribution channels

(2) Estimate the number of storage tanks nationwide

- Assume the average tanks size is 10,000 gallons
- Assume the average turnover time is 3 weeks

$$\text{Number of tanks} = 356 \text{ MM lbs} \left(\frac{\text{gal}}{11.1 \text{ lb}}\right)\left(\frac{1 \text{ tank}}{10{,}000 \text{ gal} \times 17}\right) = 280 \text{ tanks}$$

(3) Estimate storage emissions (fixed roof tanks)

Breathing Loss

$$L_B = 1.02 \times 10^{-5}\, M_v \left(\frac{P}{14.7-P}\right)^{0.68} D^{1.73}\, H^{0.51}\, T^{0.5}\, F_p\, CK_x$$

$$L_B = 1.02 \times 10^{-5}\, (85) \left(\frac{5}{14.7-5}\right)^{0.68} (10)^{1.73}\, (9)^{0.51}\, (1.15)(0.5)(1.0)$$

L_B = 0.23 Mg/yr

Working Loss

$$L_W = 1.09 \times 10^{-8}\, M_v P V N K_n K_c$$

$$L_W = 1.09 \times 10^{-8}\, (85)(5)(10{,}000)(17)(1)(1)$$

L_W = 0.79 Mg/yr

Total Loss

$L_T = L_B + L_W$ = 1.0 Mg/yr per tank

Total nationwide storage emissions = (1.0)(280) = 280 Mg/yr where:

M_v = molecular weight of product vapor (lb/lb mole)

P = true vapor pressure of product (psia)

D = tank diameter (ft)

H = average vapor space height (ft)

T = average diurnal temperature change (°F)

F_p = paint factor (dimensionless); 1.0 for clean white paint

C = tank diameter factor (dimensionless):

for diameter $\geq$ 30 feet, C = 1

for diameter < 30 feet, $C = 0.771D - 0.013D^2 - 0.1334$

K_c = product factor (dimensionless) = 1.0 for VOL

V = tank capacity (gal)

K_n = turnover factor (dimensionless):

for turnovers > 36, $K_n = \frac{180 + N}{6N}$

for turnovers $\leq$ 36, $K_n = 1$

(4) Estimate container filling emissions

Loading Loss

$$L_L = 12.46 \frac{S\ T\ M}{R}$$

where: S = saturation factor (0.50 for submerged fill and 1.45 for splash fill)

T = True vapor pressure, psia

M = Molecular weight

R = Temperature, °R

Assume 50 percent splash filling (S = 1.0)

$$S = (0.5)(0.5) + (0.5)(1.45) = 1.0$$

$$L_L = 12.46\left(\frac{(1.0)(5)(85)}{530}\right) = 10.0 \text{ lb}/10^3 \text{ gal}$$

$$= 4.5 \text{ lb}/10^3 \text{ gal}$$

$$530\ 10^6 \text{ lb}\left(\frac{\text{gal}}{11.1 \text{ lb}}\right)\left(\frac{4.5 \text{ kg}}{10^3 \text{ gal}}\right) = 210 \text{ Mg/yr}$$